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7/25/68

THE APPLICATION OF BRILLOUIN SPECTROSCOPY TO SOLUTIONS OF MACROMOLECULES AND INORGANIC COMPLEXES

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

By

Frank Ignatius San Filippo

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

in the School of Chemistry

Georgia Institute of Technology

June, 1971

THE APPLICATION OF BRILLOUIN SPECTROSCOPY TO SOLUTIONS OF MACROMOLECULES AND INORGANIC COMPLEXES

Approved:

Chairman

Date Approved by Chairman: June 7, 1971

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to Dr. G. A. Miller for his guidance, tolerance, and encouragement during the course of this research.

Much gratitude is also extended to the members of the reading committee, Dr. J. A. Bertrand and Dr. R. A. Pierotti, for their cooperation and frequent advice.

Thanks are extended to Dr. W. M. Spicer for providing a teaching assistantship during the course of this work, and to the National Science Foundation and the Rayonier Corporation for fellowship support during a portion of the work.

I am especially grateful to my wife, Darlene, for her encouragement and sacrifices during this endeavor.

Finally, to those special members of my family, Mary and Pepino, and Grace and Mario, I wish to express my sincere thanks for their guidance, encouragement, understanding, and material aid that enabled me to obtain the foundation for this work.

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SUMMARY

An investigation of the reliability of the "high" or "low" value of the scattering power of benzene, coupled with a study of the solution structure of a series of acetylacetonate complexes, was initiated employing the technique of Brillouin scattering. The light scattering results were interpreted based on a thermodynamic approach relating the intensity ratio of the unshifted to the Doppler-shifted scattering with the composition derivative of the chemical potential. Scattering spectra were obtained as a function of concentration using a 6328 Å He-Ne laser source and a Fabry-Perot interferometer.

The molecular weight of standard sample 705 polystyrene (National Bureau of Standards) was determined in dilute benzene and toluene solutions. Coupling these results with a previous molecular weight determination by the conventional light scattering method has provided additional, indirect evidence supporting a "high" value of the Rayleigh ratio of benzene.

Preparations and analyses of acetylacetonate complexes were made. The compounds studied included the anhydrous and dihydrated acetylacetonates of magnesium, cobalt, and nickel, and the corresponding methoxo derivatives of these complexes.

Molecular weights were determined in coordinating and noncoordinating solvents. Ultraviolet, visible, infrared, proton resonance, and mass spectral data were collected.

It was found that the Brillouin method may be employed for the

determination of the solution structure of small solute molecules in absorbing systems where the loss of light is as high as 60 per cent.

It was found that the dihydrated magnesium acetylacetonate is trans octahedral in the solid state. The corresponding anhydrous complex is monomeric in the vapor phase. In coordinating solvents, such as methanol and DMF, magnesium acetylacetonate dihydrate is monomeric. In noncoordinating solvents, $Mg(C_5H_7O_2)_2$ is polymeric and there is a critical dependence of the molecular weight on traces of water. Methylene chloride solutions of $Mg(C_5H_7O_2)_2$ saturated with water are unstable with respect to the insoluble dihydrate.

In coordinating solvents nickel acetylacetonate dihydrate is monomeric. The anhydrous complex, $Ni(C_5H_7O_2)_2$, is polymeric in noncoordinating solvents with the molecular weight dependent upon the amount of coordinating impurities. Solutions of $Ni(C_5H_7O_2)_2$ in carbon tetrachloride, when saturated with water, are unstable with respect to the insoluble dihydrate.

In coordinating solvents cobalt acetylacetonate dihydrate is monomeric.

Magnesium methoxoacetylacetonate, $Mg(C_5H_7O_2)(CH_3O)(H_2O)$, is unstable in solution. The complex disproportionates to the diacetylacetonate and magnesium methoxide. On the basis of similar observations, it is believed that the cobalt and nickel analogs are also unstable in solution.

This work has been the first research employing the Brillouin scattering method for the determination of solute molecular weights.

CHAPTER I

INTRODUCTION

When matter is illuminated by a monochromatic beam of light, a small but detectable part of the light is scattered in all directions. The scattered light contains two components which are distinguished by their scattering mechanism. The light scattered with relatively large frequency shifts, and accounting for only a very small percentage of the total light scattered, is the Raman radiation. This effect results from interaction of the illuminating source with quantized rotational and vibrational levels of individual molecules. Typically, the minimum Raman frequency shift is in the range of 1-10 cm^{-1}. The scattered light having the same frequency as the incident light combined with scattered radiation of small frequency shift (a few tenths of a reciprocal centimeter) has been collectively denoted as Rayleigh scattering. The Rayleigh scattering is caused by density fluctuations in the medium and is by far the dominant effect in the liquid state, accounting for approximately 99 per cent of all the scattered light (1).

The spectrum of Rayleigh scattered light, referred to as the Brillouin spectrum, consists of an unshifted Rayleigh peak and two Doppler-shifted Brillouin satellites. The Brillouin peaks result from pressure fluctuations that propagate as sound waves, and fluctuations which relax by thermal processes and therefore do not propagate, give rise to the unshifted scattering.

Brillouin Scattering

The fine structure of Rayleigh scattering from macroscopically homogeneous liquids was first studied theoretically by Leon Brillouin in 1922 (2). Brillouin predicted that the spectrum should consist of a doublet whose components are shifted symmetrically from the incident frequency. Investigations by Gross in 1930 (3), and subsequently by many others, verified Brillouin's prediction, but also revealed the central unmodified component. Initially the Rayleigh line was believed to be an experimental artifact, but its existence persisted even with the most carefully controlled experimental conditions.

Landau and Placzek in 1934 (4) explained the triplet structure and calculated the ratio of intensity of the unmodified to modified components on the basis of thermodynamic fluctuation theory. According to Landau and Placzek, the displaced lines are attributed to the Doppler shift of the scattered radiation which is reflected from the system of Debye sound waves excited by thermal energy (pressure fluctuations at constant entropy). The unmodified line is due to the scattering of light by thermal motions which are unorganized in time, i.e., they are not propagated in the form of waves (entropy fluctuations at constant pressure). The ratio of the intensity of the Rayleigh line, I_C, to that of the Brillouin doublet, $2I_B$, is given by

$$I_C/2I_B = \gamma - 1 \qquad (1)$$

where γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume.

Subsequent experiments with various liquids at times confirmed and sometimes contradicted the Landau-Placzek (LP) equation. Gross (5) investigated the Brillouin scattering in several liquids and concluded that the prediction of Landau and Placzek was verified. However, for a number of other liquids, e.g., benzene, the center line was found to be more intense than that given by the LP formula (6). Many additional investigations were carried out by Fabelinskii and co-workers (7-11) in Russia; by Meyer and Ramm (12,13), and Birus (14) in Germany; by Rao (15), Bai (16), Venkateswaran (17), and Krishnan (18) in India; and by Rank (19,20) in the U.S.A. However, the Brillouin effect was difficult to observe since the small wavelength shifts and the low intensity of scattering were not readily measured with conventional light sources. Consequently, the experiments were extremely time consuming, the data obtained was rather crude, and the subject remained relatively obscure.

With the invention and development of laser sources and high-resolution interferometric techniques it has become possible to measure the Brillouin spectrum with remarkable accuracy. As a result, a surge of activity has developed since the first studies of the Brillouin effect using laser radiation appeared in 1964 (21,22).

At present the theory of Rayleigh scattering from density fluctuations is well developed for liquids that deviate from the Landau-Placzek formula (23,24). An increase in the LP ratio can occur as a result of any dispersion mechanism which causes a degree of freedom to become inaccessible to the Brillouin wave or oscillation (25). There is a transfer of energy from the propagating to nonpropagating modes, thereby decreasing the intensity of the side peaks and enhancing that of the central peak.

The total scattered intensity is unaffected by the dispersion, thus the summed intensity of the three peaks remains the same as that predicted by thermodynamic theory.

In 1967, Miller (26) extended the thermodynamic theory of Brillouin scattering to include binary solutions. He developed formulas relating the intensity ratio of the unshifted to the Doppler-shifted scattering with the composition derivative of the chemical potential in a manner similar to the Einstein-Smoluchowski (27) formula for total isotropic light scattering. In a subsequent paper (28) he extended this treatment to the study of weight average molecular weights in solution.

Since concentration fluctuations only contribute to the unshifted central component of the scattered light, the intensity of the Brillouin peaks may be used as a reference. Thus, the need to measure the incident intensity as is commonly done in the conventional scattering technique may be avoided. This offers an interesting new approach to the study of the intensity of light scattered by solutions and forms the basis of this research.

Conventional Light Scattering

In 1944 Debye (29,30) pointed out the utility of light scattering for studying the geometry and thermodynamics of macromolecules in solution. Since that time a tremendous number of investigations dealing with this technique have been reported (31). The principal object of these measurements has been the determination of the weight average molecular weight of polymers.

The theory and practice of the conventional light scattering from liquids and solutions does not take account of the frequency distributions

of the scattered light. In the determination of the weight average molecular weight of macromolecules in solution by the conventional technique, the ratio of the intensity of the scattered light to that of the incident light beam is the experimental quantity to be determined. Since the scattered light is many orders less intense than the incident beam, this ratio is difficult to measure, and it is common practice to avoid this difficulty by measuring intensities relative to some standard substance of known scattering power, such as benzene. For measurements of this type it is imperative that reliable values be determined for the absolute scattering power of standard substances.

The values of the scattering power of benzene, expressed either as the Rayleigh ratio or the turbidity, as determined by different workers, fall into two groups, the "high" and the "low" values (32). The two groups differ by some 40 per cent. The same is true for other standard substances used in calibration. Since the experimental error in the determination of the absolute scattering power is probably 25 per cent at most (32), there is obviously a systematic error present in one of the two sets of investigations.

Kratohvil and co-workers (31) have critically reviewed the literature on the calibration of light scattering instruments. They conclude that the weight of the evidence points to the so-called "high" values. However, because of the difficulty of the experiments themselves and the number of complex factors involved, it appears that there is no clear-cut procedure for adequately solving the problem on this basis.

Statement of the Problem

The first problem undertaken for this thesis was to experimentally determine the molecular weight of a generally available standard polymer sample with the objective of providing indirect evidence for either the "high" or "low" value of the scattering power of benzene. This pragmatic approach to the absolute intensity problem would avoid the thorough analysis of the geometric optics and the critical inspection of the experimental arrangement that is required in the conventional method.

As a second part, the problem included an investigation of the solution structure of a series of inorganic complexes. Several compounds in this series possess absorption bands in the visible region and the successful application of the Brillouin technique to such typical systems would provide a valuable tool for the study of inorganic complexes.

The inorganic compounds included in this study are listed in the following section along with a summary of related investigations.

Inorganic Complexes

It has been recognized for some time that a knowledge of the molecular association of solute molecules is a vital element in the understanding of the chemistry of many inorganic complexes. Typically, structural assignments for compounds in solution have been primarily based upon isopiestic, ebulliometric, and cryoscopic measurements. All of these colligative methods yield a number average molecular weight and are characterized by their sensitivity to small molecular weight constituents. On the other hand, light scattering provides the weight average molecular weight, which is more heavily weighed by higher molecular weight components.

In addition, the use of the latter method for the study of molecular systems has the added advantage that the system under study is not affected by the measurement.

The compounds chosen for this study included the anhydrous and dihydrated acetylacetonates of magnesium, cobalt, and nickel, as well as the corresponding methoxo derivatives of these compounds. Both the cobalt and nickel complexes have absorption bands in the visible region. The crystal structure has been established for the cobalt and nickel compounds, but the magnesium complex has received little attention. Some work has been done on the solution structure of anhydrous and dihydrated cobalt and nickel, and also on the methoxo derivatives of all three metal acetylacetonates.

The solid dihydrate of cobalt acetylacetonate, $Co(C_5H_7O_2)_2 \cdot 2H_2O$, is monomeric with the two water molecules coordinated in trans positions (33). The corresponding anhydrous compound exists as a tetramer in the solid state (34). Single crystal x-ray determination shows a tetrameric arrangement of $Co(C_5H_7O_2)_2$ units containing bridging and nonbridging acetylacetonate rings.

In coordinating solvents* the cobalt attains the octahedral arrangement by coordinating two solvent molecules, and the compound exists as a monomer (35). In noncoordinating solvents the anhydrous cobalt acetylacetonate is reported to exist as dimers, trimers, and possibly higher

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* Defined here as a solvent which increases the coordination number of a dissolved complex by association with the complex or one which displaces other ligands, and remains coordinated to the complex when the latter is isolated from solution.

oligomers with an apparent concentration dependence of the association number (36). However, there is indication that the apparent concentration dependence may be the result of coordinating impurities (34).

Mass spectral studies (35) of anhydrous nickel acetylacetonate, $Ni(C_5H_7O_2)_2$, have confirmed that the complex is monomeric in the vapor phase. X-Ray work (37) has established that the crystalline anhydrous compound contains trimeric units in which the association is accomplished by bridging with the pentanediono oxgyen atoms in the same manner as that for the cobalt analog. The hydrated complex, $NiA_2 \cdot 2H_2O$, is monomeric in the solid state (38).

In noncoordinating solvents it appears that the anhydrous complex, NiA_2, favors a particular associated species. The compound is reported to exist in carbon tetrachloride as trimeric units (39). In coordinating solvents the trimeric units are probably dissociated and present entirely as the solvated species (40).

The solid state structures for the anhydrous and dihydrated magnesium acetylacetonates have not been determined. However, complexes which contain six-coordinate magnesium have been reported (41).

The methoxo derivatives of cobalt, nickel, and magnesium acetylacetonate were first prepared by Bertrand and Caine (42). The metal chelates, $M(C_5H_7O_2)_2$, react with base in methanol to produce the insoluble methoxo compounds of general formula, $M(C_5H_7O_2)(OCH_3)$ (solvent).

A tetrameric structure was proposed (43) on the basis of the NMR of the magnesium complex (42) and spectral studies that indicate that the methoxide ion can act as a bridging group (44). However, the cobalt compound has been found to be highly associated in solution, a value

above 4000 was found for the molecular weight in chloroform using a vapor pressure osmometer (42). Furthermore, Kaplan (43) reports, on the basis of number average molecular weight measurements, that the methoxo complexes associate over a range of from four to eight with the association number dependent on concentration.

Subsequent to the completion of this work, Bertrand, et al. (45) reported the crystal structure of the methoxo derivatives of cobalt and nickel. By x-ray single-crystal studies they determined that both compounds, of formula $M(C_5H_7O_2)(OCH_3)(CH_3OH)$, are tetrameric in the solid state with association via methoxide bridging.

CHAPTER II

THEORY

In the classical theory of light scattering in dense media developed by Einstein and Smoluchowski (27), the scattering system is divided into volume elements V of linear dimension small compared to the wavelength of the light, but large enough to contain many molecules. The incident light beam, of intensity I_0 and polarized with the electrical vector perpendicular to the plane of scattering, will be scattered as it passes through the volume element by fluctuations in the dielectric constant, ε, such that the intensity of the scattered light, I, at a distance r from the volume element is given by

$$I/I_0 = (\pi^2/r^2\lambda^4)V^2\langle(\Delta\varepsilon)^2\rangle \ , \qquad (2)$$

where λ is the wavelength of the incident light and $\langle(\Delta\varepsilon)^2\rangle$ is the mean-square fluctuation of the dielectric constant about its mean value in the volume element.

According to the thermodynamic approach to Brillouin scattering developed by Miller (26), fluctuations in the dielectric constant are separated into propagating and nonpropagating components. Pressure fluctuations at constant entropy propagate as sound waves, giving rise to Doppler-shifted scattering. Fluctuations in entropy at constant pressure relax by thermal processes and do not propagate, thus giving rise to

unshifted scattering. In solution there are also concentration fluctuations. Since they relax by diffusion processes and do not propagate, they also contribute to the unshifted scattering.

From thermodynamic fluctuation theory (46) it may be shown that adiabatic pressure fluctuations do not mix with entropy and composition fluctuations, i.e., $\langle(\Delta S \Delta P)\rangle = \langle(\Delta n_2 \Delta P)\rangle = 0$, where S is the entropy, P the pressure, and n_2 the number of moles of solute. Thus, the propagating component of the mean-square fluctuation in the dielectric constant is given by

$$\langle(\Delta\varepsilon)^2_{adiab}\rangle = (\partial\varepsilon/\partial P)^2_{S,n_2}\langle(\Delta P)^2\rangle. \tag{4}$$

Using the result from thermodynamic fluctuation theory for the mean-square fluctuation in pressure, this component may be expressed as

$$\langle(\Delta\varepsilon)_{adiab}{}^2\rangle = (kT^2/C_V)(1-1/\gamma)(\partial\varepsilon/\partial T)^2_{P,n_2} + (2kT^2\alpha/\beta_T C_V)(\partial\varepsilon/\partial T)_{P,n_2}(\partial\varepsilon/\partial P)_{T,n_2} + (kT/V\beta_S)(\partial\varepsilon/\partial P)^2_{T,n_2}, \tag{5}$$

where T is the absolute temperature, α the isothermal coefficient of expansion, β_T the isothermal compressibility, β_S the adiabatic compressibility, C_P the heat capacity at constant pressure, C_V the heat capacity at constant volume, and $\gamma = C_P/C_V$. Since the total scattered intensity, I, is equal to the sum of the Rayleigh and Brillouin peaks, $I = I_R + 2I_B$, the

intensity formula for the two Brillouin peaks is obtained by substituting Eq. [5] into

$$2I_B/I_o = (\pi^2/r^2\lambda^4)V^2\langle(\Delta\epsilon)_{adiab}{}^2\rangle. \tag{6}$$

The sum of the intensities of the Brillouin and Rayleigh peaks may be calculated by expressing the mean-square fluctuation in the dielectric constant in terms of fluctuations in the temperature, pressure, and moles of solute. Again, the fluctuations in the thermodynamic quantities are calculated from fluctuation theory and the total average fluctuation in the dielectric constant is given by

$$\begin{aligned}\langle(\Delta\epsilon)^2\rangle = {} & (kT^2/C_V)(\partial\epsilon/\partial T)^2_{P,n_2} + \\ & (2KT^2\alpha/\beta_T C_V)(\partial\epsilon/\partial T)_{P,n_2}(\partial\epsilon/\partial P)_{T,n_2} + \\ & (kT/V\beta_S)(\partial\epsilon/\partial P)^2_{T,n_2} + \\ & (kT)(\partial\epsilon/\partial n_2)^2_{T,P}/(\partial\mu_2/\partial n_2)_{T,P},\end{aligned} \tag{7}$$

where μ_2 is the chemical potential of the solute.

The total contribution to the central peak is obtained by subtracting Eq. [5] from Eq. [7] to give

$$\begin{aligned}\langle(\Delta\epsilon)^2_R\rangle = {} & (kT^2/C_P)(\partial\epsilon/\partial T)^2_{P,n_2} + \\ & (kT)(\partial\epsilon/\partial n_2)^2_{T,P}/(\partial\mu_2/\partial n_2)_{T,P}.\end{aligned} \tag{8}$$

The intensity formula for the Rayleigh peak is obtained by substituting Eq. [8] into

$$I_R/I_o = (\pi^2/r^2\lambda^4)V^2\langle(\Delta\varepsilon)^2{}_R\rangle. \tag{9}$$

The ratio of the intensity of the Rayleigh peak to that of the two Brillouin peaks is

$$J = I_R/2I_B = \langle(\Delta\varepsilon)^2{}_R\rangle/\langle(\Delta\varepsilon)^2{}_{adiab}\rangle. \tag{10}$$

For an ideal, binary solution having a solute mole fraction x_2, the intensity ratio is given by

$$J = ((T/C_p)(\partial n/\partial T)^2 + (x_1x_2/RT)(\partial n/\partial x_2)^2)/ \tag{11}$$

$$((T/C_v)(1-1/\gamma)(\partial n/\partial T)^2 +$$

$$(2T\alpha/\beta_T C_v)(\partial n/\partial T)(\partial n/\partial P) +$$

$$(1/v\beta_s)(\partial n/\partial P)^2) ,$$

where R is the gas constant, v is the molar volume, and n is the refractive index. The partial differentiation always concerns the triad P, T, and x_2. A good approximation for many liquids is that

$$(\partial n/\partial P) \cong -(\beta_T/\alpha)(\partial n/\partial T) \tag{12}$$

which leads to the simplified form

$$J = (\gamma-1) + (\gamma-1)Kx_1x_2, \tag{13}$$

where

$$K = C_p(\partial n/\partial x_2)^2/RT^2(\partial n/\partial T)^2. \tag{14}$$

For a pure liquid, where the concentration term is absent, Eq. [13] leads to the Landau-Placzek formula

$$J = \gamma-1. \tag{15}$$

Deviations from the Landau-Placzek formula can arise from the failure of Eq. [12] and from relaxation effects where propagating fluctuations couple with internal modes in a way that enhances the central peak (23,24,25). For a dilute solution, the first term in Eq. [13], γ-1, can be replaced by J_o, the experimental intensity ratio of the pure liquid. The γ-1 in the second term is replaced by a parameter, B, that will be used to take the above deviations into account,

$$J = J_o + BKx_1x_2. \tag{16}$$

Considering the possible error involved in introducing Eq. [12], Coumou, et al. (47) have introduced the parameter

$$x = 1 + \beta_T(\partial n/\partial T)/\alpha(\partial n/\partial P),$$

which becomes zero if Eq. [12] holds exactly. Equation [11] may be rewritten in terms of x by means of a factor

$$f = (2x)/(1-x) + (\gamma x^2)/(1-x)^2 \qquad (17)$$

to give a form of Eq. [16] in which

$$J_0 = B = (\gamma-1)/(1+f\gamma) \simeq (\gamma-1)/(1+2\gamma x). \qquad (18)$$

Coumou has measured x for several organic solvents. Typically, x is in the range 0.01-0.05, which means that J_0 and B are some 2-10 per cent less than γ-1.

Considering now the deviation due to relaxation effects in a dilute solution, the spontaneously generated sound waves, as represented by the pressure fluctuation term, transfer energy to nonpropagating modes. The energy is transferred to the entropy fluctuations, but not to the concentration fluctuations. This has been confirmed by a dynamical calculation of the spectrum (85), to be resonable for dilute solutions. There is, therefore, an increase in the intensity of the central peak at the expense of the Brillouin peaks. However, the summed intensity of the three peaks remains the same as that predicted by thermodynamic theory. For dilute solutions in which the solvent is a relaxing liquid, the intensity ratio is then given by Eq. [16] with

$$B = (\gamma-1)(J_0+1)/\gamma(1+f). \tag{19}$$

The quantity B may be determined empirically using solutes of known molecular weight or calculated from literature values of x, C_p, and γ.

Scattering From Polymer Solutions

With regard to scattering from polymer solutions, Eq. [16] may be written as

$$J = J_0 + BKMc, \tag{20}$$

where M is the weight average molecular weight, J_0 is the value of J for the pure solvent, c is the weight concentration of polymer, and B and K are the constants defined in the previous section. Using the conventional concentration units of grams of polymer per milliliter of solution, Eq. [14] becomes

$$K = C_p(\partial n/\partial c)^2/RT^2(\partial n/\partial T)^2, \tag{21}$$

where C_p is the heat capacity at constant pressure of one ml of solvent.

That M is the weight average molecular weight may be demonstrated by considering Eq. [20] for a polydispersed polymer sample. When all solute species do not have the same molecular weight, Eq. [20] becomes

$$J = J_0 + BK\Sigma M_i c_i. \tag{22}$$

By definition, the weight average molecular weight is given by

$$\bar{M}_w = \Sigma n_i M_i^2 / \Sigma n_i M_i = \Sigma c_i M_i / \Sigma c_i , \qquad (23)$$

where n_i is the number of moles of species i, M_i is the molecular weight of species i, and c_i is the concentration of species i. Thus, the sum given in Eq. [22] is equal to $\bar{M}_w \Sigma c_i$, which is the same as the term given in Eq. [20] since $\Sigma c_i = c$.

In contrast, the average molecular weight obtained from colligative methods is the number average and is defined by

$$\bar{M}_n = \Sigma n_i M_i / \Sigma n_i = \Sigma c_i / \Sigma (c_i / M_i). \qquad (24)$$

A comparison of the number average with the weight average is a measure of the polydispersity of the polymer sample (48).

For real polymer solutions it is common to express the chemical potential of the solvent, μ_1, in the form of a virial equation

$$\mu_1 - \mu_1^0 = -RTV_1 c(1/M + A_2 c + A_3 c^2 + \ldots), \qquad (25)$$

where V_1 is the partial molar volume of the solvent, and A_2 and A_3 are the second and third virial coefficients. Equation [20] then takes on the form

$$BKc/J - J_0 = (1/M + 2A_2 c + 3A_3 c^2 + \ldots). \qquad (26)$$

A plot of $BKc/J - J_0$ versus c gives a curve whose limiting slope is determined by the value of A_2 and whose intercept at infinite dilution gives the reciprocal of the weight average molecular weight.

Scattering From Inorganic Solutions

In principle, light scattering can be used to determine molecular weights of almost any magnitude. A disadvantage, however, is that the sensitivity decreases with a decrease in molecular weight. This may be partially offset by the appropriate choice of solvent such that the solutions exhibit a large refractive index increment. On the other hand, when the objective is simply to distinguish between monomer, dimer, or higher oligomers, high precision is not required. In any event, the Brillouin technique is expected to yield more accurate results than the conventional method since the former avoids the added uncertainty inherent in the method of calibration.

The problem of interpreting light scattering measurements from colored solutions was treated by Mie (49) in his analysis of scattering from spheres. The theory for both scattering methods is based on the assumption that no absorption occurs. However, Mie has shown that the only change required in the theory is that the refractive index be replaced by the complex refractive index, $n(1-i\kappa)$, where κ is the index of attenuation and may be related to the absorption coefficient defined by the Beer-Lambert law (50). One may evaluate the effect of absorption by comparing the imaginary part of the complex refractive index with the real part. In order to have a detectable amount of light scattered, $n\kappa$ is negligible compared to n for reasonable incident intensities. Therefore

no modification is required in the theory. However, with the conventional method it is necessary to carefully apply Beer's law corrections to the intensities of the incident and scattered light before the required ratio of these intensities at the scattering point can be obtained (51). Since all three peaks of the spectrum of scattered light are attenuated to the same degree by absorption in the Brillouin method, no Beer's law correction is needed.

The molecular weights for the complexes are determined by measuring J as a function of concentration in a similar manner as that for the polymer solutions. The molecular weight is calculated from the slope of J versus c,

$$J = J_o + BKMc \tag{27}$$

$$dJ/dc = BKM. \tag{28}$$

The small correction factor given by Eq. [17] is omitted here since x is generally unknown and not important when an uncertainty of about 10 per cent in molecular weight is permissible.

CHAPTER III

EXPERIMENTAL

Chemicals

The following chemicals were obtained as ACS certified grade, unless otherwise specified, and were employed without further treatment.

Acetone

Benzene

Camphor

Carbon tetrachloride

Chloroform

Cobalt (II) chloride hexahydrate

1,2-Dichloroethane

N,N-Dimethylformamide

Ethanol (95 per cent)

Magnesium metal (ribbon)

Methanol

Methylene chloride

Naphthalene

Nickel (II) chloride hexahydrate

Nitric acid

2,4-Pentanedione (practical)

Potassium hydroxide

Silver nitrate

Sodium acetate trihydrate

Preparation of Compounds

The methods employed for the preparation of the compounds used in this investigation follow closely the procedures established by other workers. However, the actual composition of several compounds did not correspond to that which was reported.

Some of the preparations were carried out several times since large amounts were required for analysis and subsequent preparations, as well as the light scattering measurements. Little effort was directed toward maximizing the reaction product yields and percentage yields were not determined. However, yields were generally good.

The identity and purity of the dried compounds were established by analysis of the elements and solvated material. Although melting points were taken, they were not significant for characterization because of thermal decomposition at or below the melting point.

Carbon-hydrogen analyses were obtained from Galbraith Laboratories, Inc., of Knoxville, Tennessee. Metal analyses were obtained either gravimetrically or by EDTA titration and the identity and quantity of solvated material was determined by gas chromatography (F & M Model 720 with dual polypak-2 columns) and thermal gravimetric analysis (Mettler Thermoanalyzer-2).

Typical results are discussed in each case.

Polystyrene

Since one of the objectives of this work was to provide additional, indirect evidence supporting either the "high" or "low" value of the scattering power of benzene, it was necessary to obtain a well characterized polymer sample previously employed in the conventional light

scattering method so that the results of this work could be compared with a molecular weight determination by the conventional method.

Standard sample 705 polystyrene obtained from the National Bureau of Standards was employed in the conventional method with benzene as standard (52). In addition, this anionically polymerized sample was well characterized by osmometry, conventional light scattering, sedimentation equilibrium, viscosity, and fractionation measurements. The polymer has a narrow molecular weight distribution (ratio of weight average molecular weight to number average molecular weight equals 1.07) and a weight average molecular weight of 179,300 (53).

The sample was utilized without additional treatment.

Magnesium Complexes

The procedure employed for the synthesis of magnesium acetylacetonate dihydrate, $Mg(C_5H_7O_2)_2 \cdot 2H_2O$, was essentially that of Kaplan (43). Magnesium ribbon (0.25 mole) in approximately one inch strips was added to an excess of 2,4-pentanedione ($\sim$ 100ml) in a 500 ml erlenmeyer flask equipped with a magnetic stirrer. The mixture was stirred at room temperature until conversion of the metal was complete - approximately 48 hours. The procedure referenced above called for refluxing the reaction mixture. This resulted in the formation of a certain amount of polymeric material which made purification of the product difficult. Extending the reaction time at room temperature was considerably effective in reducing the amount of undesirable material.

The white reaction product was then recrystallized several times from methanol until the pure crystals were obtained. In view of the method of preparation and the solvent utilized for recrystallization,

this product was expected to be methanolated. However, analysis has shown that there is a great affinity for the water available in the methanol and starting material such that the crystals obtained were $MgA_2 \cdot 2H_2O$. (The conventional abbreviation, A, is used for the acetylacetonate ligand).

The crystals were then dried under vacuum at room temperature for approximately one hour and stored in a vacuum desiccator. No desiccant was employed since it was previously determined that over a period of time the desiccant would remove the water of hydration.

Confirmation of composition was made by analysis of the magnesium, carbon, hydrogen, and water content. Water was determined by dehydrating the compound in a vacuum oven at 100^0 C and collecting the solvent in a cold trap. The solvent collected was then analyzed by gas chromotagraphy on a previously calibrated polypak-2 column and identified as water. The percentage of hydrated water was determined by thermal gravimetric analysis and found to be 14.3 per cent. The calculated percentage is 13.9 per cent.

Gravimetric analysis of the anhydrous material gave 10.8 per cent magnesium and Galbraith reported 53.9 per cent carbon and 6.4 per cent hydrogen for a sample of this material. The calculated values are 10.9, 54.0, and 6.3 per cent, respectively.

The anhydrous samples of the diacetylacetonate of magnesium utilized in the light scattering experiments were simply prepared by heating the dihydrate at 100^0 C <u>in vacuo</u>.

The methoxo derivative of magnesium acetylacetonate was synthesized according to the method of Bertrand and Caine (42). However,

the compound that we obtained for each preparation was the hydrated complex, $MgA(CH_3O)(H_2O)$, and not the methanolated compound, $MgA(CH_3O)(CH_3OH)$, as reported.

To a 0.007 mole sample of MgA_2 dissolved in 350 ml of refluxing methanol, a solution of potassium hydroxide in methanol (0.007 mole in 100 ml) was added dropwise over a period of one hour. The reaction mixture was kept at reflux for a total of two hours and the product was filtered from the hot solution. The white crystals were then washed with a small amount of methanol, dried in a vacuum oven at room temperature for approximately one hour, and stored in a vacuum desiccator without desiccant.

The fact that this complex is hydrated was established by gas chromotagraphy in a manner similar to that employed for $MgA_2 \cdot 2H_2O$. The percentage of hydrated water was determined by thermal gravimetric analyses and found to be 10.2 per cent. The calculated percentage is 10.4 per cent.

Gravimetric analysis of $MgA(CH_3O)(H_2O)$ gave 14.3 per cent magnesium and Galbraith reported 41.0 per cent carbon and 7.3 per cent hydrogen. The calculated values are 14.1, 41.8, and 7.0 per cent, respectively.

The anhydrous material, $MgA(CH_3O)$, was analyzed for magnesium by EDTA titration and found to contain 16.3 per cent metal. The calculated percentage is 15.8 per cent.

Nickel Complexes

The nickel (II) acetylacetonate dihydrate was prepared according to the method of Fernelius and Bryant (54). To a solution of 0.25 mole

$NiCl_2 \cdot 6H_2O$ in 250 ml of water was added a solution of 0.50 mole 2,4-pentanedione in 100 ml of methanol, while stirring with a magnetic bar stirrer. A solution of 0.50 mole sodium acetate trihydrate in 100 ml of water was then added and the resulting mixture was heated for a short period. After cooling in an ice bath for several hours, the blue crystals of $NiA_2 \cdot 2H_2O$ were filtered, washed with a small amount of water, and dried.

The percentage of H_2O was determined gravimetrically and found to be 12.2 per cent. The calculated percentage is 12.3 per cent.

The green anhydrous material utilized in the light scattering experiments was prepared by heating $NiA_2 \cdot 2H_2O$ at 100^0 C in vacuo. A sample of the dihydrate was sent to Galbraith Laboratories with instructions to dehydrate before carbon-hydrogen analysis. They reported 44.2 per cent carbon and 5.7 per cent hydrogen which is a little low in carbon and a little high in hydrogen. It was previously determined in this laboratory that the dihydrate is relatively difficult to dry completely and it is therefore believed that their analysis sample was not completely free of water. The calculated percentages are 46.7 per cent carbon and 5.4 per cent hydrogen.

The methoxo derivative of nickel (II) acetylacetonate may be prepared by the same method utilized in the case of magnesium. This compound was not prepared, however, since it was determined on the basis of preliminary measurements, made on a sample obtained from Dr. J. A. Bertrand (55), that this complex is unstable in solution.

Cobalt Complexes

The analogous cobalt (II) complexes may be prepared by the same procedures

outlined above. These compounds were not prepared however, since only a limited number of measurements were made on this system and small quantities of the complexes were also obtained from Dr. Bertrand.

Light Scattering Experiments

All light scattering measurements were made at a scattering angle of approximately 90^0 as shown in Figure 1. A He-Ne laser was used as the light source and the scattered light was resolved with a scanning Fabry-Perot interferometer. The intensity of the resolved light was measured with a photomultiplier detector and the Brillouin spectra were displayed on a X-Y recorder. The details of the instrument are described below.

The Instrument

This Brillouin scattering photometer has been described in the literature (28). However, in view of additional modifications that were made it seems profitable to give a general description.

A Perkin-Elmer Model 6320 He-Ne laser provided 10-mW radiation at 6328 $\mathring{A}$ with a half-width of about 0.025 cm^{-1}. The laser which emits vertically polarized light was mounted on an optical bench and separately housed in a wooden case. The cell, optics, and photomultiplier were also mounted in a wooden case set perpendicular to and at a distance of approximately 10cm from the light source. The inside of both compartments were painted black to minimize stray light.

The sample was contained in a standard square turbidity cell made by the Phoenix Precision Instrument Company. The cell was surrounded by a close fitting, electrically heated aluminum block and the temperature

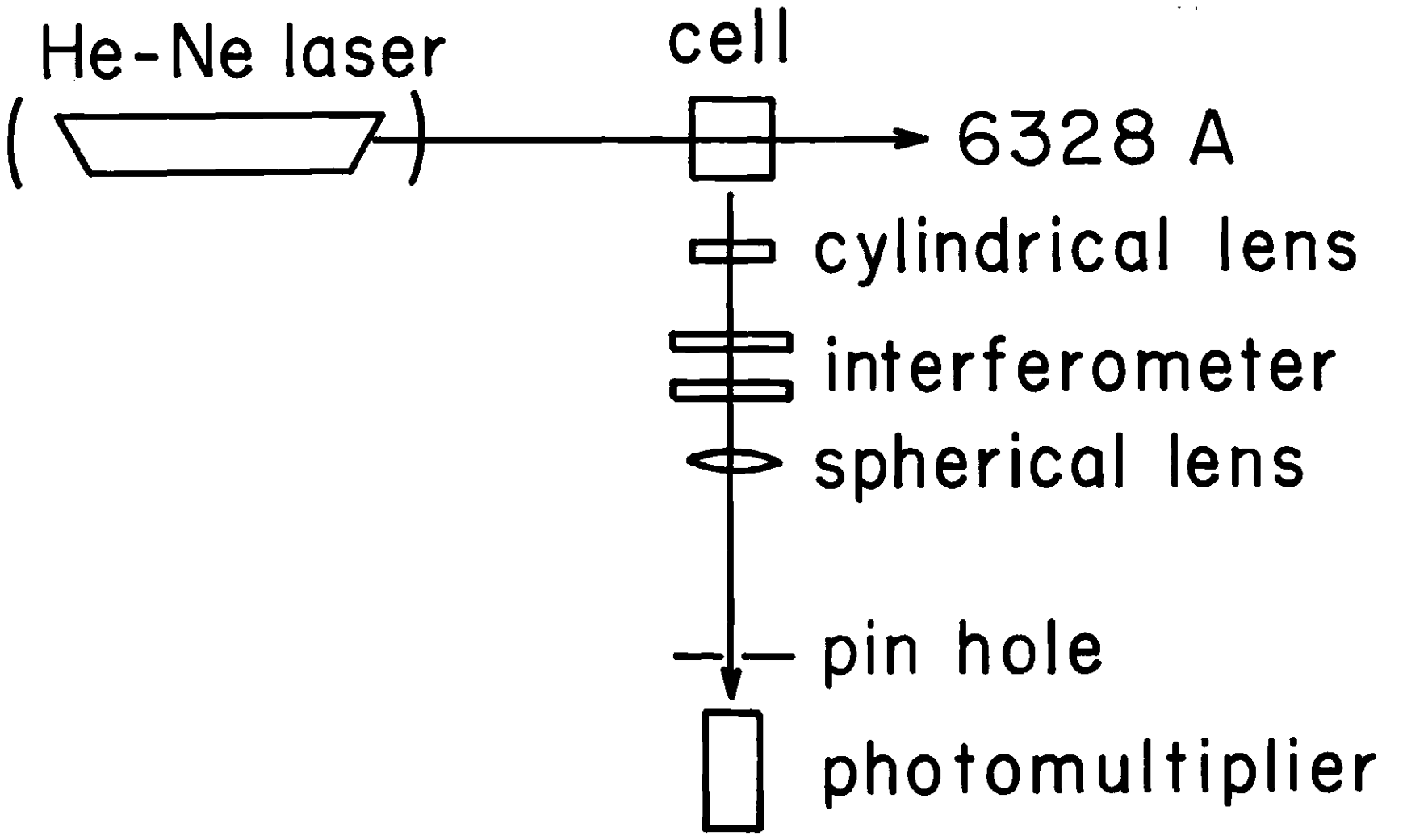

Figure 1. Schematic of Light Scattering Apparatus

of the sample was measured by a thermocouple attached to the cell assembly. Melting ice was used as a reference junction and the thermocouple output was measured with a potentiometer. In addition, the entire room housing the instrument was thermostatted. The sample temperature was maintained at 25 $\pm$ 1^{0} C. A fluctuation of two degrees in temperature was found to have neligible effect on the intensity ratio.

The laser light was brought to a focus within the cell by means of a spherical lens attached on the outerside of the optical housing. The scattered light was gathered with a cylindrical lens of 10-cm focal length, which served to collimate the light parallel to the horizontal plane only. This assembly was converted to a spherical lens for measurements with absorbing complexes since more light could be gathered by focusing on a small region immediately within the cell.

The scattered light was analyzed with a piezoelectrically driven, scanning Fabry-Perot interferometer. A simplified sketch of the interferometer is shown in Figure 2. The mounting consisted of two 95 per cent reflectant mirrors, one of which was attached to the piezoelement and the other to an orthogonal assembly with micrometer adjustment for parallelism. The mirror spacing, d, was set at 11mm. The voltage drive for the interferometer consisted of a stablized 350-V power supply coupled with a 10-turn, 250,000-ohm Helipot driven by the multispeed output of a synchronous motor. The same ramp voltage provided the signal for the X axis of the recorder.

Light emerging from the interferometer was focused by a 50-cm focal length spherical lens onto a pinhole which passed only the central spot

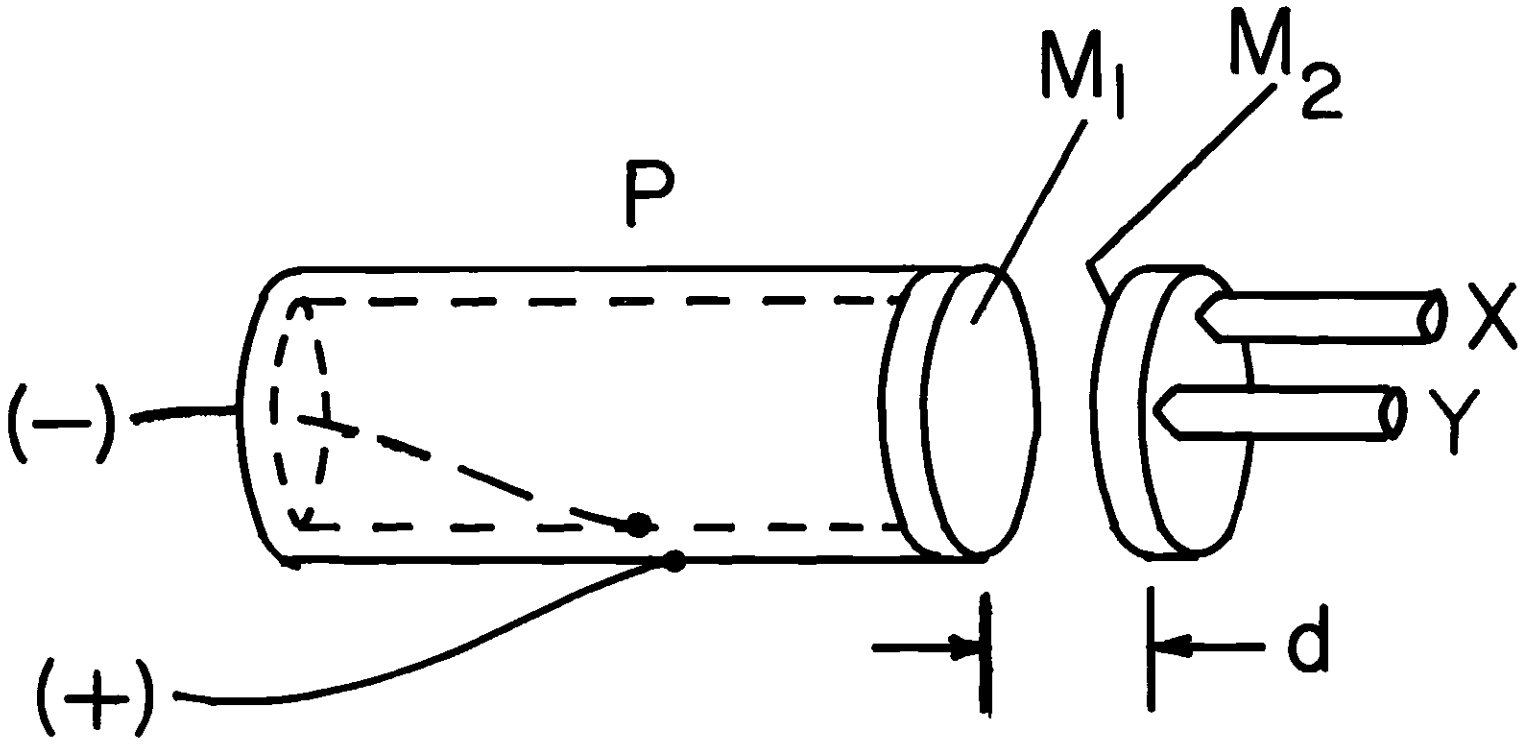

Figure 2. Simplified Diagram of Scanning Fabry-Perot Interferometer Showing Piezoelectric Ceramic Tube (P), Multilayer Dielectric Mirrors (M_1, M_2), Micrometer Adjustment for Parallelism (X, Y). Mirror Spacing (d) is adjustable.

of the interferometer ring system. Light emerging from the pinhole passed through a rotatable nicol prism and was gathered by an EMI 9592-B photomultiplier with an S-10 response. The signal was amplified through a Schoeffel M-600 photometer and was displayed on a Hewlet-Packard Model 7005AM X-Y recorder.

Preparations of Solutions

The solutions were generally prepared by dissolving a weighed amount of sample in a volumetric flask, with the more dilute solutions being prepared by aliquots. The concentrations usually ranged between 0.1×10^{-3} and 30.0×10^{-3} grams of sample per cubic centimeter of solution. Generally, four or five solutions were prepared for each sample with amounts chosen in such a way to effect approximately equal spacing with respect to concentration. The final gravimetric analysis for each solution was determined after the light scattering measurements by evaporating aliquots to dryness and weighing.

Prior to making the scattering measurements, the turbidity cell was first washed free of dust with the condensing vapors of boiling solvent, and the solution (or solvent) to be studied was then filtered immediately into the cell. The fabricated cell cleaner was basically a distillation apparatus with the cell serving as the condensor. The solvents and solutions were made dust free by filtration through a millipore or sintered glass filter under a positive pressure of nitrogen. Several solutions required repeated filtration to remove the dust. Some of this dust came from the walls of the cell and could not be removed by the condensing vapors, thus the main purpose of repeated filtration was to wash

the dust from the cell. The effectiveness of the filtration procedure was assessed by either placing the cell in the laser beam and visually observing any residual dust or from occasional spikes in the spectra. When the filtration was determined to be incomplete, the above process was repeated.

Collection of Data

After the solution (or solvent) was sufficiently dust-free, the cell was carefully placed in the cell assembly of the instrument and allowed to remain there for a short period. This allowed the cell and its contents to come to thermal equilibrium and provided time for some residual dust to settle out from the scattering volume. At this point it should be mentioned that the removal of dust is not the problem that it has sometimes been made out to be. Consider for example the preparation of dust-free water, a solvent which is perhaps one of the most difficult to clarify. Kratohvil and co-workers (56) have considered this problem from two points of view: first, they compared their data and that of several others in the literature for the scattering from water and although the data was obtained from water prepared by a variety of clarification procedures, the results did not bear any relationship with the particular clarification method employed. Secondly, they estimated the number and size of particles that would have to be present in order to affect significantly the observed scattering of water. Their calculations were based on typical materials found in dust, such as polymer latexes, silica, silicates, and cellulosic materials, and found that an impossibly large number of particles, of sizes that would certainly be visually apparent, would have to be present in order to affect the measurements.

In obtaining the spectrum for a typical sample, it was first necessary to establish the correct base line. This was accomplished by measuring the photomultiplier output with the laser off, thus obtaining the dark current base line. Then the spectrum of the anisotropically scattered light was scanned through the nicol prism set to pass horizontally polarized light. Since the Brillouin spectrum was scanned with the prism set for vertically polarized light, the correct base line was four-thirds the intensity of the horizontal component of the scattered light (57). A typical recorder trace of a spectrum is given in Figure 3.

In all cases studied here the depolarized spectrum was too broad to be resolved by the interferometer and gave a relatively constant intensity over the entire free spectral range of the interferometer. For some solutions at higher concentrations, as in Figure 3, it was necessary to expand the photometer scale to read accurately the area under the Brillouin peaks.

The Rayleigh peak was divided from the Brillouin peaks by drawing vertical lines at the minimum where they overlap and the area under the Brillouin peaks was terminated with vertical lines through the minimum points on the trace between successive orders. The areas marked off were then measured with a planimeter.

The procedure described above was repeated for each solvent and solution, and the experimental intensity ratios thus obtained were recorded for each system investigated.

Auxiliary Experiments

Refractive Increments

For each system the constant K, given by $(C_p/RT^2)[(\partial n/\partial c)/(\partial n/\partial T)]^2$,

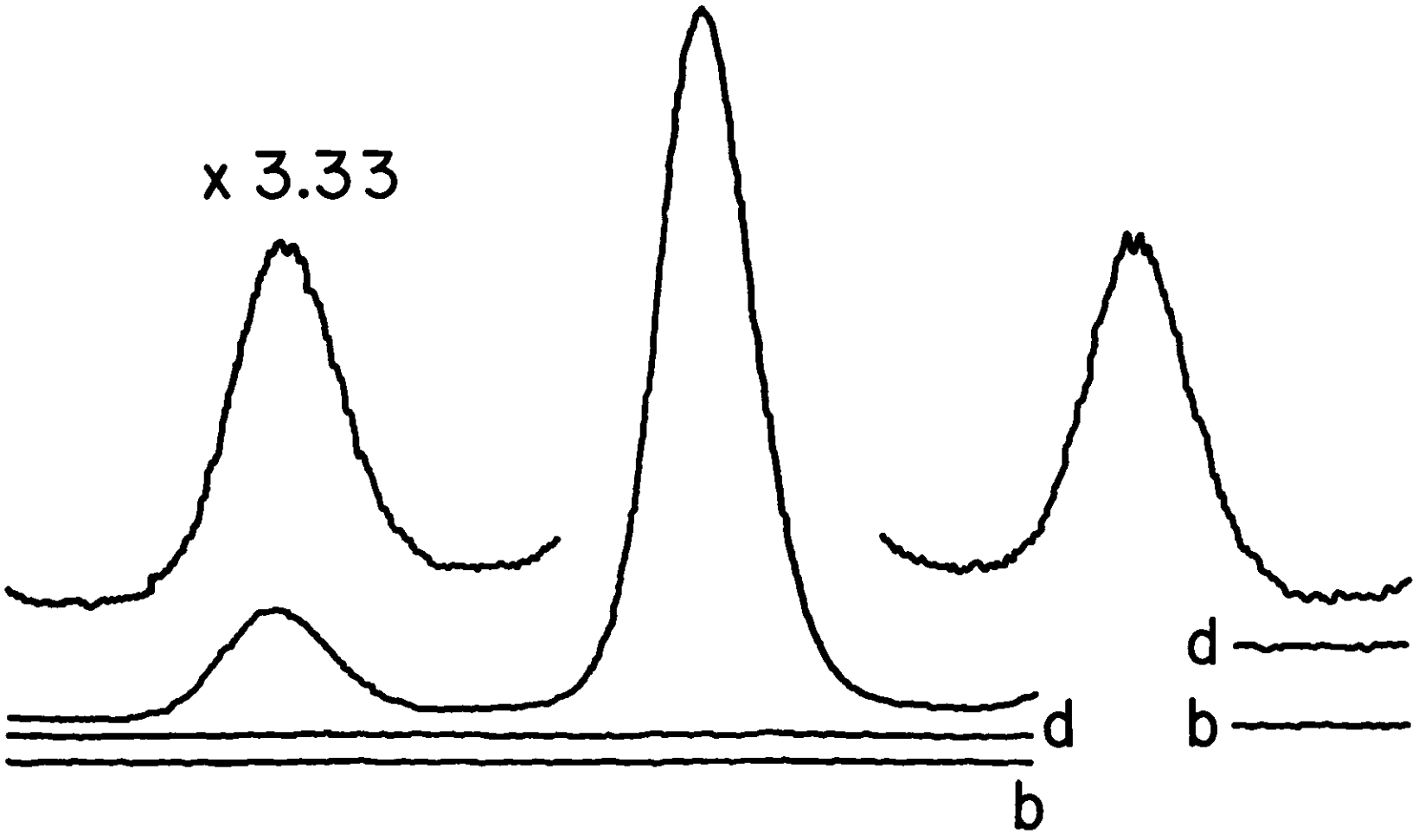

Figure 3. Spectrum of Light Scattered by Polystyrene 705 in Benzene at 25^0 with Dark Current Base Line (b) and Horizontal Component of the Depolarized Spectrum (d); c = 3.41 x 10^{-4} g/ml. The Side Peaks are Separated 0.17 cm^{-1} from the Central Peak.

is determined by independent measurements. For all of the solvents employed, the heat capacities were obtained from the literature. In some instances the concentration or temperature dependence of the index of refraction was also available, however this data was limited and in most cases both quantities were measured.

For the systems $MgA_2 \cdot 2H_2O$ - DMF, $MgA_2 \cdot 2H_2O$ - CH_3OH, $MgA(CH_3O)(H_2O)$ - CH_2Cl_2, and $MgA(CH_3O)(H_2O)$ - CH_3COCH_3, the measurements of the concentration dependence of the index of refraction, $\partial n/\partial c$, were made with an unmodified Brice-Phoenix Differential Refractometer (58) using the laser as the illuminating source. This instrument is designed to measure directly small differences in refractive index, Δn, between two liquids by the deflection method. It has been shown by Brice and Haliver (58) that Δn is directly proportional to the deflection of the slit image, Δd, and that the proportionality constant can be established either by geometrical means or by performing measurements on suitable liquids of known refractive index. This instrument was calibrated by Smith (52) using water and aqueous solutions of sucrose (59) at the sodium D line. By using the magnifications for three wavelengths, which were given in the Brice-Phoenix manual, the proportionality constants for 5460 $\mathring{A}$, and 4358 $\mathring{A}$ were calculated and their values along with the value for the sodium line were extropolated (assuming $k = a/\lambda^2+b$) to 6328 $\mathring{A}$ to obtain $k = 9.90 \times 10^{-4}$. The proportionality constants were assumed to be independent of temperature.

All other $\partial n/\partial c$ and $\partial n/\partial T$ values measured were determined on an Abbe'-type Bausch and Lomb precision refractometer using the laser as the illuminating source. A standard test piece and conversion tables were

provided by the manufacturer and the values of n were interpolated to 6328 $\overset{0}{A}$ by assuming $n = a/\lambda^2+b$.

For the system $MgA_2 \cdot 2H_2O$ - DMF, both instruments were used and the values of $\partial n/\partial c$ were in good agreement.

Spectral Measurements

The ultraviolet and visible spectra were measured at 25^0 C with a Cary Model 14 Recording Spectrophotometer using matched quartz cells of 0.997 centimeter light path length. The solutions measured were all approximately 10^{-5}M and extinction coefficients were calculated from $\epsilon = (\log I_0/I)/(0.997 \times c)$.

The infrared spectral data were collected with a Perkin-Elmer Model 237B Grating Infrared Spectrophotometer using nujol mulls. All of the spectra were qualitative and the 1944 cm^{-1} peak of polystyrene was used as the standard reference point.

Proton resonance spectra were obtained using a 100MH_z Jeolco Model 4H-100 instrument with tetramethylsilane as internal standard.

Mass spectral data were obtained with a Varian Model M66 medium resolution instrument.

CHAPTER IV

RESULTS AND DISCUSSION

In view of the natural division between the two systems investigated in this study it seems logical to divide the results into two groups. The weight average molecular weight of standard polystyrene 705, second virial coefficients, and the conclusions drawn with regard to the scattering power of benzene are reported in the first section of this Chapter. The light scattering results along with other experimental data on the inorganic complexes are reported in a separate section.

Standard Polystyrene 705

As can be seen from Eq. [26], the riciprocal of the molecular weight is given by the limit of $BKc/J-J_0$ as the concentration approaches zero. The second virial coefficient, A_2, may be obtained by taking one-half of the initial slope of the $BKc/J-J_0$ versus c curve. Thus, in order to obtain these quantities from the experimental intensity ratios, the data must be extrapolated to zero concentration.

The experimental intensity ratios, given in Table 1, were linear with concentration and therefore were assumed to obey Eq. [26] with the third and higher virial coefficients equal to zero. In order to facilitate the calculations, the quantity $c/J-J_0$ was plotted versus concentration as shown in Figure 4.

The molecular weight was calculated from $M = [(c/J-J_0)_0 BK]^{-1}$ and the second virial coefficient was obtained from the relationship

Table 1. Experimental Intensity Ratios, J, for PS 705 at 25^0 C.

Solvent	10^4c, g/ml	J
Benezene	0	0.86
	1.05	1.34
	2.31	1.91
	3.41	2.39
	7.17	3.84
	9.75	4.87
	14.98	6.13
Toluene	0	0.43
	1.56	1.12
	2.38	1.53
	4.76	2.40
	7.63	3.33
	10.57	4.23
	14.70	5.22

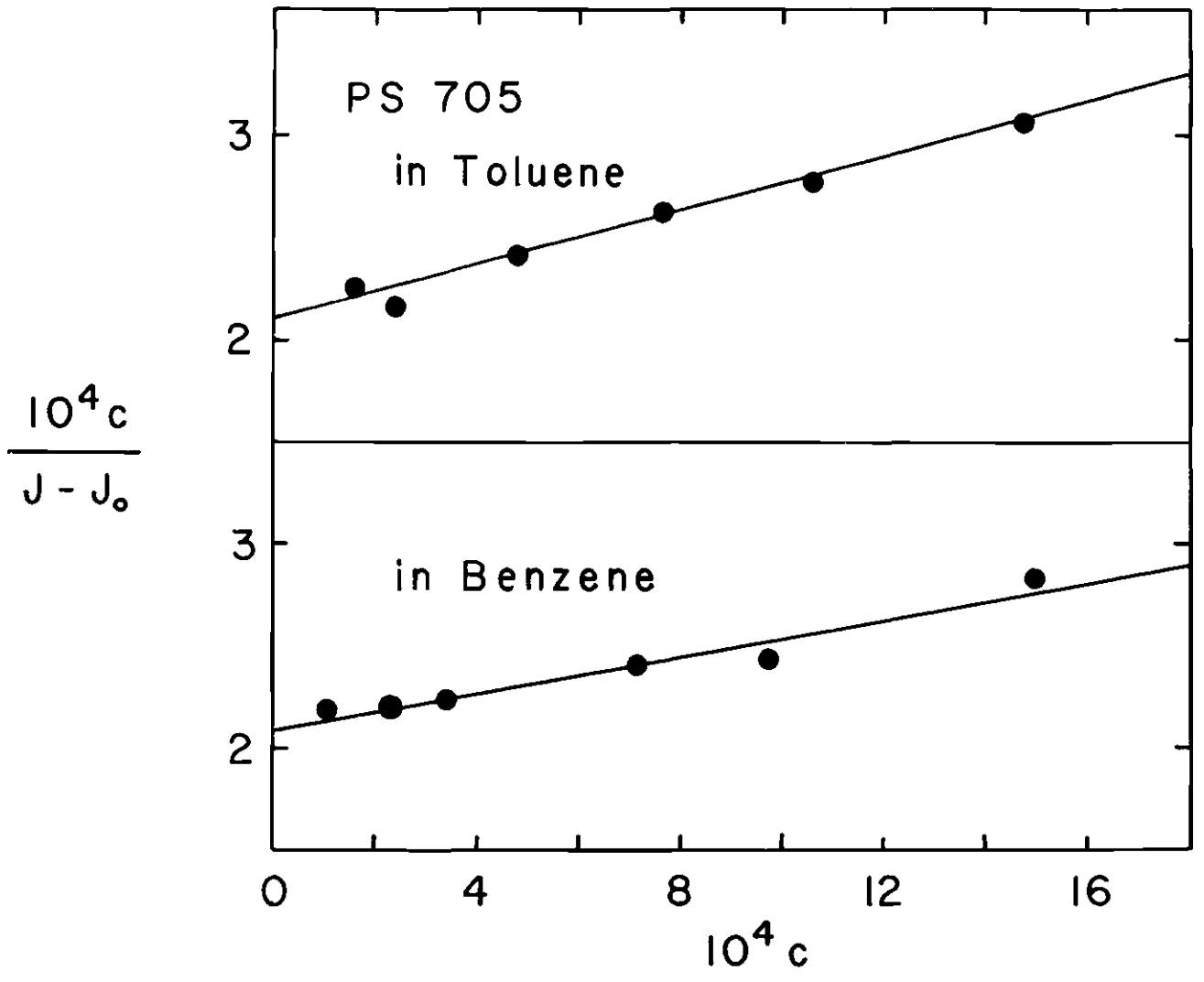

Figure 4. Intensity Ratios Plotted in Accordance with Eq. [26].

A_2 = (slope) (BK)/2, using the intercept and slope, respectively, of a least squares fit for each set of data.

The least squares fit gave, for PS 705 in benzene

$$c/J-J_0 = 2.09\times10^{-4} + 0.0453c$$

and in toluene

$$c/J-J_0 = 2.11\times10^{-4} + 0.0648c.$$

Using the parameters in Table 2 along with the limiting values of the intensity ratios, a weight average molecular weight of 1.73 x 10^5 g/mol was obtained in both solvents. The second virial coefficients are 6.2 x 10^{-4} mol ml/g^2 in benzene, and 8.8 x 10^{-4} in toluene.

The values of γ given in Table 2 were revised slightly from those in reference (28), after an extensive review of the literature. The values for each solvent represent an average obtained from $\gamma = \beta_T \rho V^2$ and $\gamma = (T\alpha^2V^2/C_p) + 1$ using data from references (60-74), where β_T is the isothermal compressibility in atm^{-1}, ρ is the density in g/ml, V is the velocity of sound in m/sec, and α is the thermal expansion in deg^{-1}.

It is rather difficult to assess the accuracy of the second virial coefficients since no directly comparable literature values appear to be available. However, on the basis of the expected behavior* for this

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* The second virial coefficient may be thought of as a measure of the interaction between the polymer and solvent. High values of A_2 indicate highly solvent swollen molecules and low values indicate that polymer - polymer contacts are preferred. When A_2 = 0 phase separation is near. For dilute solutions of polystyrene it has been shown (48) that toluene is a better solvent than benzene.

Table 2. Light Scattering Parameters at 25° C.

	Benzene	Toluene
C_p	0.3616[a]	0.3580[a]
$\partial n/\partial T$	-6.27×10^{-4}[a]	-5.51×10^{-4}[a]
$\partial n/\partial c$	0.102[b]	0.1065[b]
K	0.0542	0.0757
x	0.046[a]	0.015[a]
γ	1.431	1.350
J_o	0.86	0.43
B	0.509	0.360

[a]Reference 28; C_p is in cal/ml-deg.

[b]Extrapolated to 6328 Å and 25° C from data in reference 52 and 61.

parameter (75) coupled with a wide variety of data for polystyrene in both of these solvents (61), it is apparent that the values obtained are within the expected range. Certainly, the values are consistent relative to each other since for a given polymer sample the second virial coefficient should increase with the goodness of the solvent and, although benzene is a good solvent for polystyrene, toluene is even better.

Although both values of A_2 are within the representative domain for these systems, they are at the high end of the range and may reflect a systematic error in determining J at higher concentrations. If this is the case, the cause is probably greater overlap of the central peak with the side peaks at higher concentrations.

Table 3 lists the values of the weight average molecular weight obtained in benzene and toluene along with similar values for PS 705 from different sources. The value of M for PS 705 obtained in this work supports the "high" value for the Rayleigh ratio of benzene. This conclusion is based on the following reasoning. The molecular weight of PS 705 has been determined by Smith (52) using benzene as a scattering standard. The measurements were done at 30^0 C and three wavelengths, 5460, 4358, and 3650 $\mathring{A}$. The value of M listed in Table 3 is the average of the values obtained at these three wavelengths. The Rayleigh ratios of benzene which were chosen at these wavelengths were 17.2×10^{-6}, 48.7×10^{-6}, and 112.0×10^{-6} cm^{-1}, respectively, all at a scattering angle of 90^0. These are typical "high" values and were based on the measurements of Tomimatsu and Palmer (76), Ehl and co-workers (77), and Cantow (78). Smith's results would agree exactly with those obtained in this work if these Rayleigh ratios were lowered, on the average, by only two per cent.

Table 3. Weight Average Molecular Weight of PS 705.

Source	Solvent	Method	10^{-5}M
NBS[a]	Cyclohexane	Light Scattering	1.793
NBS[a]	Cyclohexane	Sedimentation	1.898
Ref 52	Benzene	Light Scattering	1.76
Present	Benzene	Brillouin spectrum	1.733
Present	Toluene	Brillouin spectrum	1.733

[a]Data provided with sample.

The "low" values of the Rayleigh ratio of benzene are about 40 per cent lower, hence clearly incompatible with the results obtained in this work coupled with those of Smith.

The uncertainty in the scattering data was determined from the average residuals for the least squares extrapolations to zero concentration. The average per cent deviation of the ordinate values from the least squares line reflects a precision of ± 1 per cent in molecular weight. There is an uncertainty of about ± 3 per cent in the constant B, due mainly to the uncertainty in the value of γ. The principal uncertainty in the calculation of the constant K is in the value of the refractive increment, which is estimated to be accurate to ± 2.0 per cent (52). Since K is proportional to the square of $\partial n/\partial c$, the uncertainty in K is about ± 4 per cent. Thus, the overall uncertainty in molecular weight, taking into consideration the high probability that the errors in these variables will tend somewhat to cancel one another out, amounts to ± 5 per cent. Excluding systematic errors, the A_2 values are also probably certain to ± 5 per cent. Smith (52) reports an uncertainty of ± 10 per cent in M for this polymer by the conventional method.

Inorganic Complexes

The portion of this work concerning the inorganic complexes encountered much more difficulty than was initially expected. The study was begun with the magnesium compounds in order to avoid possible complications due to absorption of primary light. It was also felt that a wide range of light scattering measurements could be accomplished on this system and thus a basis of comparison could be constructed for the other

compounds. However, it was soon apparent that the number of scattering measurements that could be made would be severely limited.

This was dictated not by the method, but rather by the limitation in appropriate solute - solvent systems due to insolubility. Many solvents suitable for light scattering measurements were tried, but the solubility of the compounds severely limited these studies to only a few. In addition, where the solubility was sufficient to measure a scattering effect, the accessible concentration range for each solvent was relatively small.

This complication coupled with those of analyses prompted additional experiments designed to assist in the confirmation of structure and establish a basis of comparison with other work on these compounds. It was also felt that other experiments would serve to distinguish whether skeptical results were due to the scattering method or to the system investigated.

Anhydrous Magnesium Diacetylacetonate

The anhydrous MgA_2 complex was perhaps the most difficult compound to study from the standpoint of obtaining scattering data. As would be expected, in coordinating solvents conversion to the monomer is essentially complete. In non-coordinating solvents solubility is extremely limited, and when the compound was found to dissolve sufficiently to obtain a measureable light scattering effect, the data clearly demonstrated a molecular weight dependence on the presence of traces of water. The dry solid may be kept exposed to the atmosphere without apparent change for periods of several hours and probably much longer, but in solution

there is a strong tendency to coordinate any water that may be present and thereby reduce the degree of association.

Light scattering measurements were made with methylene chloride solutions using two samples of MgA_2 prepared separately. The experimental intensity ratios given in Table 4 were plotted versus concentration as shown in Figure 5. The slopes were obtained by least squares fit and are listed in Table 12. The parameters for the least squares fit of the experimental data for the concentration dependence of the refractive index are also listed in Table 12. The molecular weights were calculated according to $M = (\Delta J/c)(BK)^{-1}$, using the parameters given in Table 13. The values obtained are listed in Table 14.

The scattering data suggests molecular weights at least as high as 28,000. It is also clearly indicated that no definite associated structure exists in this solvent and it appears that there is no reason to expect that the results would be any different in some other non-coordinating solvent. These observations coupled with the fact that it is extremely difficult to remove all water, precluded additional measurements since they would be of doubtful value.

The first sample, labeled A in Figure 5, was run with no special precaution to exclude water. The scatter in the intensity ratios is interpreted as reflecting the fluctuating amounts of water present in this series of samples. Several samples were tested for water content and it was found that the amounts varied between a few tenths to approximately one per cent of sample weight.

Special precautions were taken for the second run. Traces of water were removed by dissolving MgA_2 in hot CH_2Cl_2, cooling to 0^0 to

Table 4. Experimental Intensity Ratios, J, for MgA_2 in Methylene Chloride at 25^0 C.

10^3c, g/ml	J
0	0.71
9.68	1.60
17.81	2.19
24.53	1.86
26.30	1.54
29.95	1.57
0	0.71
2.47	3.06
2.90	3.29

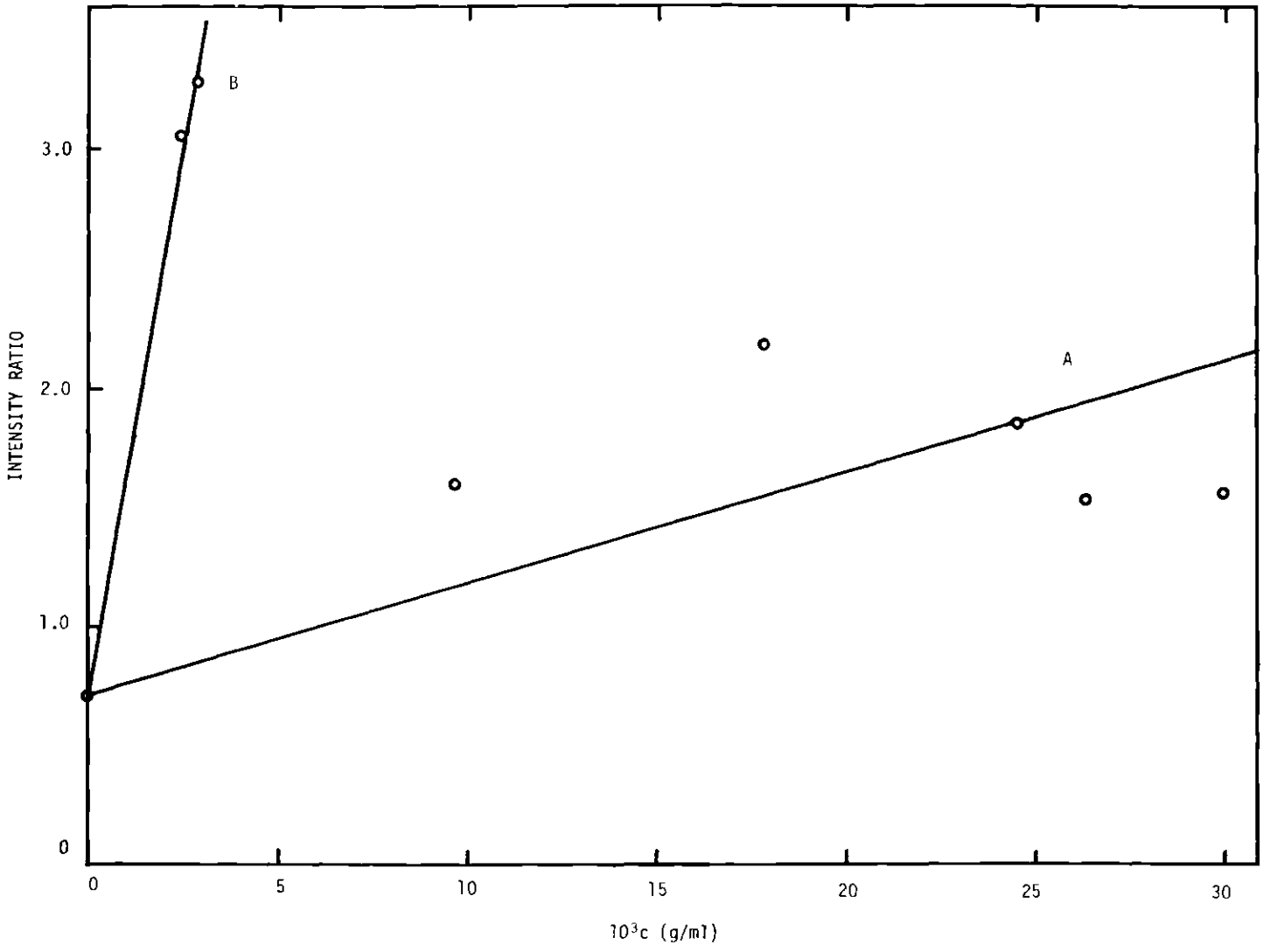

Figure 5. Intensity Ratio Versus Concentration for MgA_2 in CH_2Cl_2 at 25^0 C.

precipitate essentially all the complex, and dissolving more MgA_2 for the light scattering measurements. In addition, the solutions were isolated from the atmosphere as much as possible during the course of the measurements in an effort to minimize water contamination. The results, labeled B in Figure 5, indicated a degree of association which is considerably greater than the previous run. Only three experimental points were taken because of the difficulty involved in excluding the water, and since only an indication of the effect on association was desired. The results of the first run, plot A Figure 5, would seem to suggest a possible concentration - dependent molecular association process. However, this was discounted since such an interpretation would have to explain the scatter as a trend toward higher molecular weights at higher dilution, which is not very likely. It is possible that some dihydrate is formed as a metastable colloid which, at higher concentration, coagulates to some degree and is partially removed during filtration. In this connection, when a layer of water is placed over a solution of MgA_2 in CH_2Cl_2, the dihydrate begins to precipitate at the interface, and continues, with shaking, until complete. Hence, solutions of MgA_2 saturated with water are unstable with respect to the insoluble dihydrate.

The infrared spectrum of MgA_2 was recorded and compared with spectra in the literature (43,79). The absorption bands were found to be identical with those reported. The UV spectrum consisted of a fairly symmetrical, broad peak of relatively high intensity, with maximum absorption at 2770 Å and a slight shoulder on the long wavelength side. This is also consistent with the reported spectrum (80).

The compound decomposes to a dark brown oil at approximately 275^0 C.

The NMR absorption spectrum in CCl_4 solution was also recorded. Although solubility was limited in this solvent, a quantity of the material did dissolve and at least an indication of the spectrum was observed. The spectrum consisted of two broad absorption regions, centered at approximately 1.85 and 5.30 ppm, which contained at least three peaks in each region. These regions are consistent with the methyl and proton absorption observed for the enol form of acetylacetone.

The multiple peaks in both regions suggest unsymmetrical methyl groups and middle carbon protons of the chelate rings. This splitting phenomena has been observed with unsymmetrical tris (β - ketoenolato) complexes (52,81) where protons not equivalent by symmetry gave different chemical shift values. In addition, the chemical shift difference for non-equivalent methyl groups has been used to differentiate between cis and trans isomers (82,83). In this case the non-equivalancy of the various protons is interpreted as resulting from the unsymmetrical configurations of the chelate rings which is dictated in the process of building the long chain species. This is consistent, furthermore, with the general observation that regions of broad absorption are typical of polymeric materials.

The mass spectrum for this compound gave intense peaks at the following m/e values: 123 (100), 207 (95), and 222 (90), where the values in parentheses represent relative intensities. The spectrum was obtained with 70 V electrons at an instrument pressure of 10^{-6} torr. A sample temperature of 150^0 C was necessary to obtain the spectrum. Clearly, the

large relative intensity of the molecular ion (m/e = 222) reflects the stability of the monomer MgA_2 unit.

In view of what has been presented, it appears that the solution structure of MgA_2 in CH_2Cl_2 consists of polymers of rather high molecular weight, with a critical dependence on traces of coordinating impurities. Admittedly, a molecular weight of 28,000 appears rather high for such systems and is difficult to reconcile. Perhaps some dihydrate in the form of a metastable colloid is partly responsible for this high result.

Apparently, the chains are built up of MgA_2 units with association through sharing of β - diketone oxygens. The polymers would then have metal atoms in distorted octahedral environments. It has been reported (35) that many of the metal - A_2 type complexes associate through β - diketone oxygens and complexes containing six-coordinate magnesium are well known (41).

Since the crystalline structure of MgA_2 is not known and knowledge thereof would provide collaboration for the solution structure, an attempt was made to study the anhydrous crystals by x-ray diffraction. The solid crystals were prepared by sublimation using a drying pistol with bromobenzene. However, considerable difficulty was encountered and producing single crystals of satisfactory size and quality for x-ray work was found to be a formidable task. Only after repeated attempts at preparation were crystals of sufficient quality obtained for consideration of x-ray study. At present, over 75 crystals have been examined and we have yet to discover a crystal which is not twinned, cracked, or both.

Magnesium Diacetylacetonate Dihydrate

Since the dihydrate of MgA_2 served as precursor for the anhydrous material, several of the auxiliary measurements were omitted for this compound. The mass spectrum was identical to that of the anhydrous material, except for an initial intense peak for water. As would be expected, the compound also decomposed to a dark brown oil at approximately 275^0 C.

Crystals of good quality were grown in several solvents and some were given to Bertrand and co-workers (55) for x-ray diffraction studies. They found that the crystalline material is monomeric with the hydrated water in trans positions.

Light scattering measurements were made in methanol and DMF solutions. The experimental intensity ratios are listed in Table 5 and the data are plotted in Figure 6. Because of the limited amount of data available in the literature for DMF, a constant, α, for this solvent was determined using naphthalene as standard. This new solvent constant incorporates the previously defined solvent constant, B, as a product with the ratio $C_p/RT^2(\partial n/\partial T)^2$. Thus the data for the system $C_{10}H_8$ - DMF (given in Table 6) was utilized to calculate α from the product $(\Delta J/c)(\partial n/\partial c)^{-2}M^{-1}$, where M is the molecular weight of naphthalene. The value of α thus obtained is 4.44 mole/ml. The intensity ratios are plotted in Figure 6.

All of the scattering data and the refractive index data were fit by least squares and the results are listed in Table 12. The molecular weights, calculated from the parameters given in Table 13 and the value of α given above, are listed in Table 14.

Table 5. Experimental Intensity Ratios, J, for $MgA_2 \cdot 2H_2O$ at 25^0 C.

Solvent	10^3c, g/ml	J
Methanol	0	0.25
	2.75	0.38
	7.15	0.53
	10.90	0.62
	13.36	0.70
	25.06	1.09
N,N-Dimethylformamide	0	0.38
	2.39	0.41
	5.76	0.45
	9.55	0.50
	15.27	0.58
	25.17	0.72
	36.64	0.88

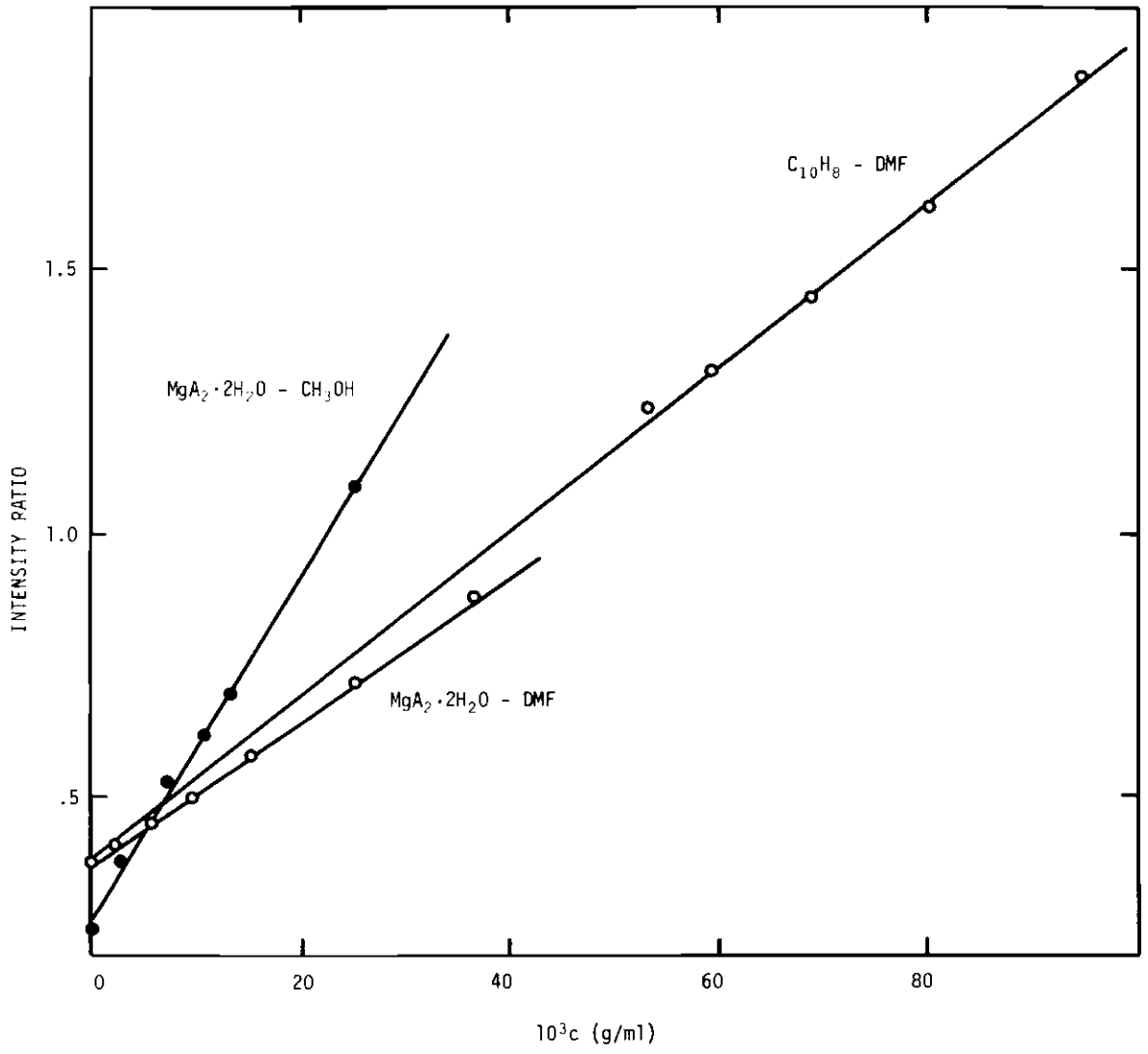

Figure 6. Intensity Ratio Versus Concentration For $MgA_2 \cdot 2H_2O$ and $C_{10}H_8$ at 25^0 C.

Table 6. Experimental Intensity Ratios, J, for Naphthalene in N,N-Dimethylformamide at 25^0 C.

10^3c, g/ml	J
0	0.38
53.12	1.24
58.87	1.31
68.94	1.45
80.20	1.62
94.75	1.87

From the average residuals for the least squares fit of the scattering data an average per cent deviation was calculated and found to reflect a precision of ±3 per cent in molecular weight. In addition, there is an uncertainty of about ±3 per cent in the solvent constant and ±4 per cent in the value of K. Thus, the calculated molecular weights are probably certain to about ±6 per cent.

Clearly, the results indicate that $MgA_2 \cdot 2H_2O$ exists as a monomer in solution ($M(CH_3OH)$ = 243, M(DMF) = 285) as well as in the crystalline form.

Magnesium Methoxoacetylacetonate

As has been the case in other structural investigations of various β - ketoenolate complexes of metals, the study of this complex ($MgA(CH_3O)(H_2O)$) has developed some interesting and unsuspected complications. It was mentioned in the previous chapter that this compound was thought to be the methanolated complex (42). In addition, on the basis of number average molecular weight determinations and spectroscopic studies (43), it was proposed that this complex associates, via methoxide bridging, over a range of from four to seven with the association number dependent on concentration. The results of this work indicate that in solution the methoxo complex is unstable.

Light scattering measurements were made in three solvents. The experimental data, listed in Tables 7 and 8, are plotted in Figure 7 and the calculated weights are listed in Table 14. Other necessary parameters have been listed in Tables 12 and 13 and the method of calculation has been previously described in this section.

Table 7. Experimental Intensity Ratios, J, for $MgA(CH_3O)(H_2O)$ at 25^0 C.

Solvent	10^3c, g/ml	J
Acetone	0	0.44
	2.92	0.99
	5.31	1.48
	7.32	1.76
	9.86	2.24
	13.19	2.74
Chloroform	0	0.69
	7.75	1.09
	12.66	1.16
	18.38	1.18
	48.24	1.53
Methylene Chloride	0	0.71
	4.41	0.97
	6.84	1.02
	10.50	1.09
	17.04	1.29
	26.65	1.65

Table 8. Experimental Intensity Ratios, J, for $MgA(CH_3O)(H_2O)$ in Methylene Chloride at 25^0 C, after refluxing for 36 hours.

10^3c, g/ml	J
0	0.71
1.89	1.03
4.18	1.28
6.35	2.07
9.76	2.82

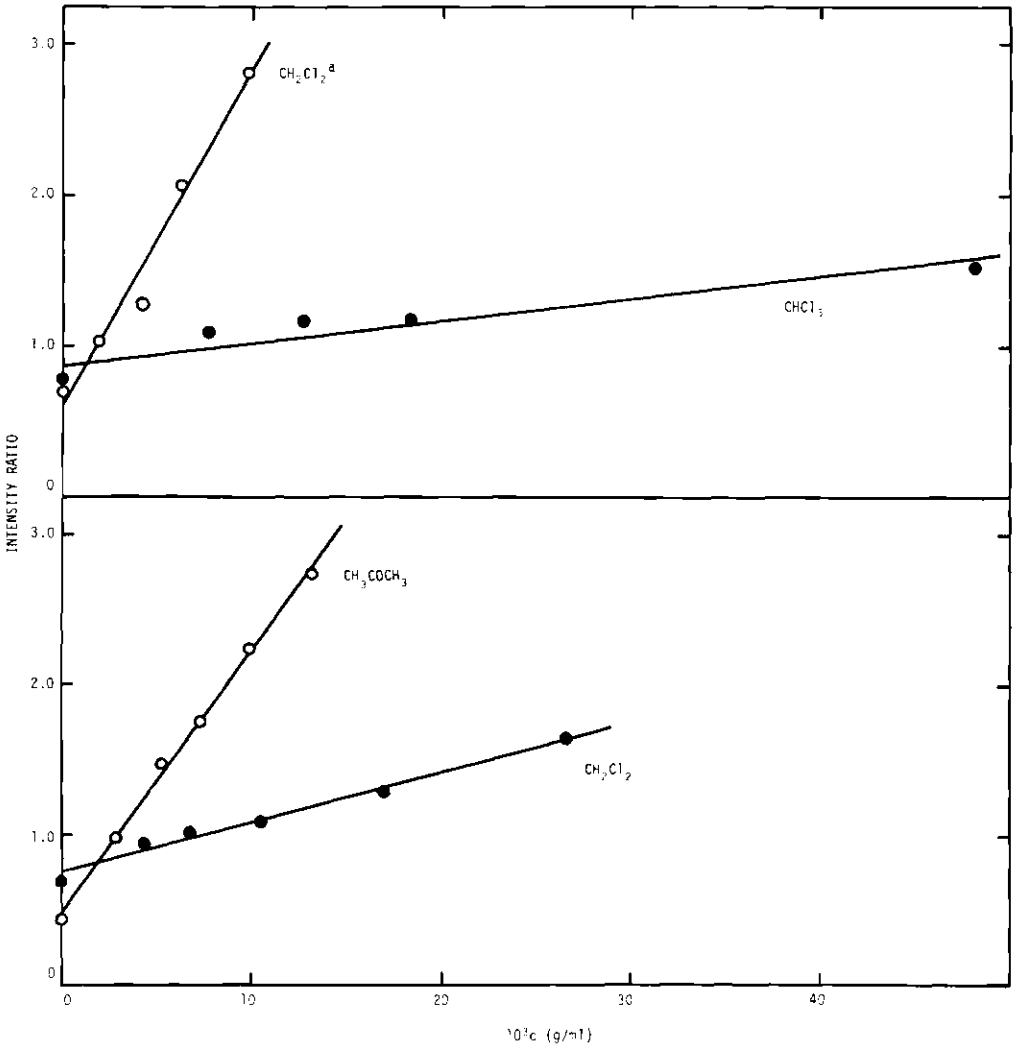

Figure 7. Intensity Ratio Versus Concentration for $MgA(CH_3O)(H_2O)$ at 25^0 C. [a]Refluxed Prior to Light Scattering Measurements.

The complex was first run in acetone and chloroform and the molecular weights seemed to be consistent with those of Kaplan (43). His results averaged around 1000 in $CHCl_3$ and for the same solvent in this work an average weight of 1880 was obtained. A higher value by the light scattering method is to be expected since this method is more sensitive to higher molecular weight species. However, our results did not indicate a concentration dependence although the concentration range was comparable.

Measurements were then made in methylene chloride solution and a lower weight average was obtained (1490). This suggested that perhaps a definite associated species of lower weight might exist with weak bridging to form the longer chains. Following this interpretation, it was decided to thermally treat a sample of the complex in methylene chloride solution in the hope that this would destroy the weak bridging and render the complex in a definite associated form. This could be verified subsequently by similar treatment in other solvents.

The results, which are also given in Figure 7, clearly indicated that this was not the case, since the molecular weight after treatment was substantially higher (8080). Furthermore, in the course of making these measurements it was found that a quantity of finely divided solid collected in the filter during clarification. Subsequent checks with the previously employed solvents lead to the conclusion that what originally was being removed as dust was the same colloidal material. These colloidal particles were of sufficient refractive index such that detection was very difficult. In addition, it was found that crystals of $MgA_2 \cdot 2H_2O$ grew from solutions of the methoxo complex in all of the solvents mentioned above.

Apparently, the methoxo complex disproportionates in the solvents employed giving a mixture of the methoxo complex with $MgA_2/MgA_2 \cdot 2H_2O$ and $Mg(OCH_3)_2/Mg(OCH_3)_2 \cdot 2H_2O$ or, just the disproportionation products if the disproportionation is complete. The results obtained for the refluxed sample are consistent with this interpretation since the heat treatment would upset the equilibrium between the disproportionation products. Apparently this favored the formation of the methoxide of magnesium since this is known to be polymeric.

The disproportionation products were confirmed by separation and analysis of the products from an acetone solution of the methoxo complex. The separation was accomplished by evaporating the solution at room temperature and selectively dissolving the diacetylacetonate in methanol. The methanol insoluble powder was analyzed for water of hydration and magnesium. The calculated percentages for water and magnesium in $Mg(OCH_3)_2(H_2O)_2$ are 29.4 and 19.9, respectively. The values found were 28.9 for water and 19.9 for magnesium. Evaporation of the methanol solution gave crystals of $Mg(C_5H_7O_2)_2 \cdot 2H_2O$ as confirmed by x-ray diffraction.

The ultraviolet spectrum of the methoxo complex in chloroform solution consisted of a broad absorption band with maximum at 2885 $\mathring{A}$ and a slight shoulder on the long wavelength side. The absorption band was practically identical to that of the diacetylacetonate with the exception of intensity. The intensity for the methoxo complex was approximately one-half that of the diacetylacetonate on a monomer mole basis. Kaplan (43) reported similar results for this complex, and attributed the reduction in intensity as resulting from the replacement of one of the

acetylacetonate rings. It seems, however, that the same result may be achieved with a mixture of one-half mole diacetylacetonate and one-half mole methoxide.

The infrared spectrum of a nujol mull of the magnesium methoxo complex was basically identical to the spectrum of the diacetylacetonate with the exception of additional peaks in the 3000 and 1100 cm^{-1} regions. This is also consistent with the spectra obtained by Kaplan. Although it is difficult to draw definite conclusions without conducting an extensive spectroscopic study of the possible compounds, it does seem plausible that the methoxo spectra could be a superposition of the diacetylacetonate and methoxide spectra. The absorption regions in the methoxo spectrum that are not present in the diacetylacetonate spectrum could possibly be assigned to the methoxide. Typical water absorption lies in the 3000 to 3500 cm^{-1} region and metal alkoxides are generally known to exhibit C-O stretchings in the 1000 cm^{-1} region (84).

The nuclear magnetic resonance spectrum was obtained in carbon tetrachloride solution and the five absorption peaks observed agreed with the spectrum report by Bertrand and Caine (42). Their assignments were made for the methoxo compound, but here again, it seems plausible that the assignments could be changed to account for the disproportionation products instead. More definitive statements can only be made after an extensive NMR study of the system.

It is particularly interesting to note that the mass spectrum of the methoxo complex is identical to that obtained for the diactylacetonate, with the exception of an initial peak for water. Furthermore, the spectrum did not exhibit a peak at a m/e value of 154, or multiples

thereof, which would correspond to the weight of the methoxo compound minus the water.

Clearly, the methoxo derivative of magnesium diacetylacetonate is unstable in solution. It is believed, on the basis of the evidence accumulated here, that upon dissolution the complex completely disproportionates. However, the possibility has not been completely ruled out that upon dissolution an equilibrium is established and complete disproportionation occurs only as one of the products is removed from solution. For example, by growing crystals of the dihydrate of magnesium diacetylacetonate. On the other hand, it would seem possible that the preparation reaction accomplishes only the conversion of the diacetylacetonate to the methoxide and the two compounds precipitate as a mixed crystal. However, this has been discounted on the basis of comparison with the diffraction patterns for the analogous nickel and cobalt compounds (55). In any event, it is evident that a complete understanding would require a substantial amount of additional experiments which would be beyond the objective of this research.

Cobalt and Nickel Methoxoacetylacetonates

In view of the results obtained for the methoxo complex of magnesium, little work was done with the corresponding cobalt and nickel compounds. Several solutions of the nickel compound were prepared and the same colloidal material was obtained as in the case of the magnesium compound. The scattering from these solutions indicated that this was also a polymeric material.

The cobalt compound has been investigated by Bertrand and Caine (42) using vapor pressure osmometry. They found that the compound was

highly associated in various solvents. A value above 4000 was obtained in chloroform.

Recently, Bertrand, et al. (45) reported the crystal structure of the methoxo derivative of cobalt and nickel. By x-ray single-crystal studies they determined that both compounds, of formula $M(OCH_3)A(CH_3OH)$, are tetrameric in the solid state.

In this study a solution of the cobalt complex in chloroform was prepared and allowed to stand for approximately 24 hours. The results were similar to the observations made with the magnesium complex. A powdery material settled and crystals grew which were of the same color and form as that for $CoA_2 \cdot 2H_2O$.

Cobalt Acetylacetonate

The anhydrous crystalline structure has been determined for cobalt (II) acetylacetonate. Using single crystal x-ray structure determination techniques, Cotton and Elder (34) found that this complex is tetrameric in the solid state. They further reported that this tetramer contains three distinct types of rings: those with both oxygens serving as bridges, those with one oxygen serving as a bridge between two cobalt atoms, and those with both oxygens bonded to only one cobalt atom. This certainly lends support to the interpretation given in a previous section for the NMR spectrum of the analogous magnesium compound.

In non coordinating solvents, Cotton and Soderberg (36) found that the anhydrous compound is polymeric with an apparent concentration dependence. However, they indicate similar complications due to coordinating impurities as was observed in this work for the anhydrous

magnesium compound. The scatter in their data suggests that perhaps the same situation exists for the cobalt compound.

It is known that in coordinating solvents cobalt acetylacetonate exist as a monomer with the cobalt octahedrally coordinated (35). Thus, it is fairly certain that the dihydrate will also exist in a coordinating solvent as a monomer. For this reason $CoA_2 \cdot 2H_2O$ was chosen as the first complex, with an absorption band in the visible region to be examined by light scattering.

A single point determination was run for the dihydrate in methanol. The parameters and data are listed in Tables 10, 13, and 14. The molecular weight thus obtained ($\bar{M}w$ = 267) agrees well with the calculated weight for the monomer (293). The effect of an absorption band in the vicinity of the incident frequency is negligible. For a more direct comparison, values of the extinction coefficient and damping factor have been calculated and listed in Table 9. Values for the concentration were taken from the most concentrated solution used in the light scattering run. The extinction coefficient for the cobalt complex was obtained from the literature (36) and converted to comparable units. Clearly, the damping factor, $n\kappa$, is negligible compared to the refractive index for the solutions considered.

Nickel Acetylacetonate

X-ray work (37) has established that crystalline anhydrous nickel acetylacetonate contains trimeric molecules in which the association is accomplished by bridging with the pentanediono oxygen atoms in the same manner as that established for the analogous cobalt compound. The dihydrate is monomeric in the solid state (38).

Table 9. Experimental Values of the Extinction Coefficient and Absorption Percentage at 6328 Å and 25° C.

	NiA_2 - CCl_4	$NiA_2 \cdot 2H_2O$ - CH_3OH	$CoA_2 \cdot 2H_2O$ - CH_3OH
c	24.07×10^{-3}[a]	16.80×10^{-3}[a]	9.40×10^{-3}[a]
ε	19.5[b]	16.2[b]	20.5[c]
A[d]	58%	40%	30%
n	1.45598	1.32845	1.32630
n_K	4.73×10^{-6}	2.74×10^{-6}	1.94×10^{-6}

[a]Taken from maximum value in light scattering measurements; c is in g/ml.

[b]Calculated from experimental optical density, path length of absorption cell, and concentration of solution used to obtain visible spectrum; ε is the ml/g-cm.

[c]Reference 36.

[d]Absorption percentage calculated for an average path lenth, in the light scattering cell, of 8.0 mm.

Table 10. Experimental Intensity Ratios, J, for $CoA_2 \cdot 2H_2O$ and $NiA_2 \cdot 2H_2O$ at 25^0 C.

System	10^3c, g/ml	J
$NiA_2 \cdot 2H_2O$ - CH_3OH	0	0.25
	3.88	0.43
	5.60	0.48
	8.40	0.57
	16.80	0.85
$NiA_2 \cdot 2H_2O$ - CCl_4	0	0.74
	5.54	0.82
	10.52	0.96
	13.83	1.07
	22.90	1.17
$CoA_2 \cdot 2H_2O$ - CH_3OH	0	0.25
	9.40	0.72

Light scattering measurements were made for the anhydrous material and the dihydrate. The experimental intensity ratios given in Tables 10 and 11 were plotted versus concentration as shown in Figure 8. The slopes were obtained by least squares fit and are listed in Table 12. The parameters for the least squares fit of the experimental data for the concentration dependence of the refractive index are also listed in Table 12. The molecular weights were calculated using the parameters given in Table 13, and the values obtained are listed in Table 14.

Initially, the dihydrate was run in carbon tetrachloride solution since experiments reported in the literature (40) indicated that this compound was soluble in this solvent. However, the molecular weight calculated for this system (M = 1010) was considerably larger than that expected. If the dihydrate did exist in this solution, it is difficult to envision association since the nickel would have to achieve a coordination number greater than six.

This point was resolved by adding approximately 15 volume per cent water to a green solution of the diacetylacetonate in carbon tetrachloride and allowing the system to come to equilibrium. After a period of time, the NiA_2 in carbon tetrachloride formed $NiA \cdot 2H_2O$ and came out of solution, leaving the colorless carbon tetrachloride as bottom layer, blue solid dihydrate as middle layer, and water as top layer. The water was slightly blue colored.

Clearly, the dihydrate, $NiA_2 \cdot 2H_2O$, is insoluble in carbon tetrachloride, and polymeric chains of NiA_2 exist in solution. The chains would be randomly terminated by coordination with water and the molecular weight would reflect the same dependence on coordinating impurities as was

Table 11. Experimental Intensity Ratios, J, for NiA_2 in Carbon Tetrachloride at 25^0 C.

10^3c, g/ml	J
0	0.74
3.80	0.84
7.60	0.91
11.40	1.06
15.82	1.22
24.07	1.52

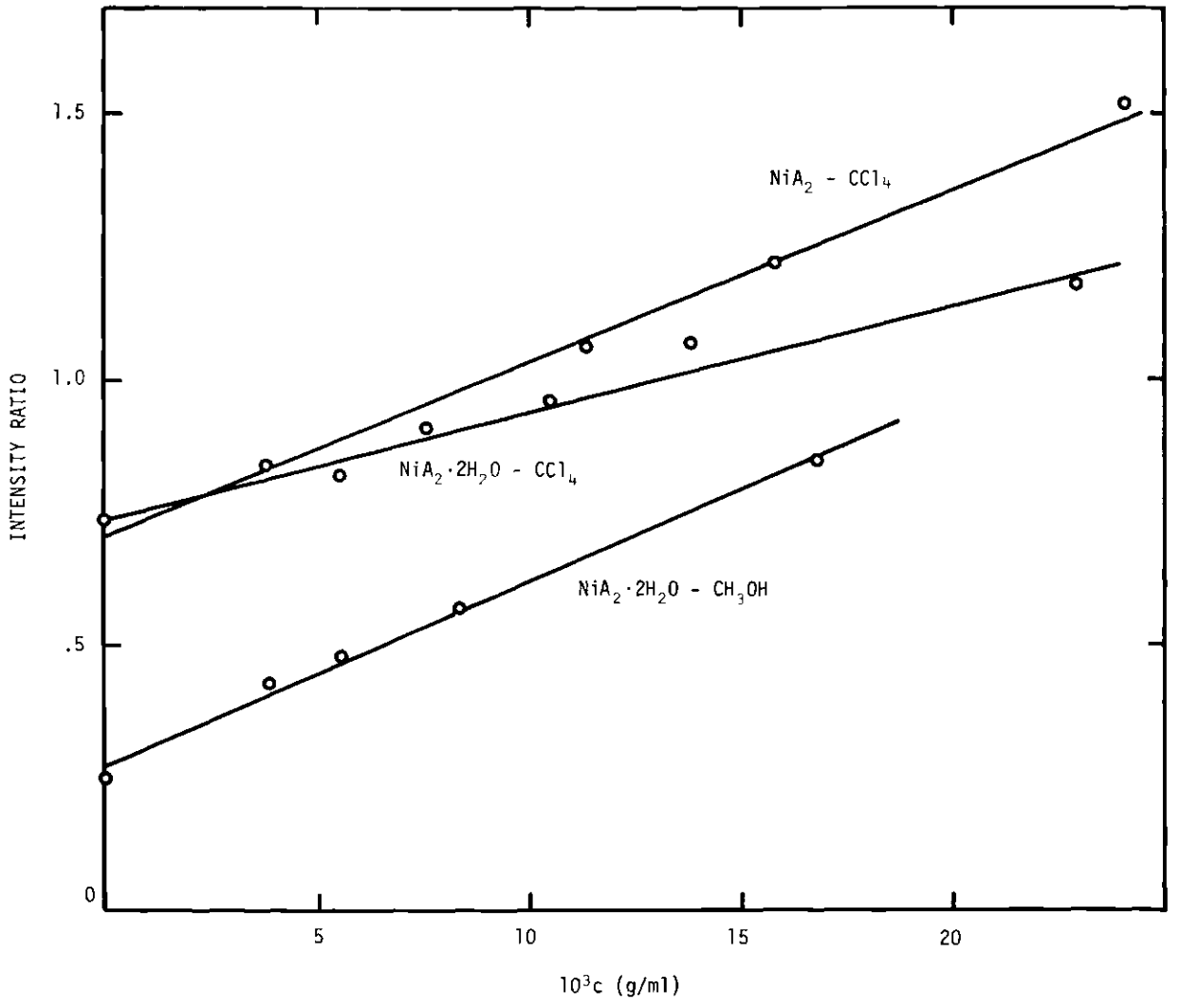

Figure 8. Intensity Ratio Versus Concentration for $NiA_2 \cdot 2H_2O$ and NiA_2 at 25^0 C.

demonstrated for MgA_2. This was verified by measuring the scattering from solutions of the anhydrous material in carbon tetrachloride. The molecular weight determined for this system was substantially higher (2200). From the data it is also apparent that no definite associated structure exists. It is interesting to note that Fackler and Cotton (39) reported that this compound exists in carbon tetrachloride as trimeric units. Their results are based on ebullioscopic measurements and therefore represent a number average molecular weight. Taken with the results of this work, the molecular weight distribution is concluded to be quite broad giving a fairly large ratio of $\bar{M}w/\bar{M}n$.

The dihydrate was also run in methanol solution where it is expected to be monomeric. The molecular weight thus determined (282) was in excellent agreement with the expected value (292).

Table 12. Parameters for Least Squares Fit of Experimental Data

System	$J=a_0 + a_1c$		$n=a_0 + a_1c$	
	a_0	a_1	a_0	a_1
$MgA_2 \cdot 2H_2O$ - CH_3OH	0.273	32.6	0.597×10^{-4}	0.190
$MgA_2 \cdot 2H_2O$ - DMF	0.374	13.7	1.42623	0.104
MgA_2 - CH_2Cl_2	0.723	91.1 x 10'	1.41940	0.0966
	0.736	83.4	1.41940	0.0966
$MgA(CH_3O)(H_2O)$ - CH_2Cl_2[a]	0.601	22.1 x 10'	1.41938	0.0887
$MgA(CH_3O)(H_2O)$ - CH_3COCH_3	0.484	17.5 x 10'	0.152×10^{-4}	0.134
$MgA(CH_3O)(H_2O)$ - $CHCl_3$	0.872	14.8	1.44014	0.0526
$MgA(CH_3O)(H_2O)$ - CH_2Cl_2	0.763	32.9	-0.326×10^{-4}	0.0798
$NiA_2 \cdot 2H_2O$ - CH_3OH	0.274	34.8	1.32540	0.182
$NiA_2 \cdot 2H_2O$ - CCl_4	0.741	19.9	1.45427	0.0815
NiA_2 - CCl_4	0.706	32.8	1.45436	0.0708
$C_{10}H_8$ - DMF	0.387	15.6	1.42622	0.166

[a]Refluxed in CH_2Cl_2 prior to light scattering measurements.

Table 13. Light Scattering Parameters at 25° C.

Solvent	J_o	γ	C_p, cal/ml-deg[a]	$10^4 \partial n/\partial T$	B^k
CH_3COCH_3	0.443	1.389[b]	o.4139[b]	-5.02[h]	0.404
CH_2Cl_2	0.709	1.521[c]	0.3748[c]	-6.0[i]	0.585
CH_3OH	0.252	1.205[d]	0.4760[e]	-3.90[h]	0.213
$CHCl_3$	0.690	1.486[d]	0.3442[f]	-6.14[h]	0.553
CCl_4	0.742	1.440[d]	0.3243[g]	-5.74[j]	0.532

[a]Densities for converting to these units came from the reference in footnote i.

[b]Reference 71.

[c]J. L. Hunter and H. D. Dardy, J. Chem. Phys., 42, 2961 (1965).

[d]Reference 60.

[e]H. G. Carlson and E. F. Westrum, Jr., J. Chem. Phys., 54, 1464 1971.

[f]J. W. Williams and F. Daniels, J. Amer. Chem. Soc., 46, 903 (1924).

[g]J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, J. Amer. Chem. Soc., 66, 1064 (1944).

[h]Measured in this laboratory.

[i]Manufacturing Chemists Association Research Project, Selected values of Properties of chemical compounds.

[j]Reference 28.

[k]Calculated from Eq. [19] assuming x in Eq. [17] to be negligible.

Table 14. Weight Average Molecular Weights of Inorganic Complexes.

Complex	Formula Weight	Solvent	∂n/∂c	K	$\bar{M}_w$
$MgA_2 \cdot 2H_2O$	259	CH_3OH	0.190	0.640	243
$MgA_2 \cdot 2H_2O$		DMF	0.104	----	285
MgA_2	222	CH_2Cl_2	0.0966	0.0550	28,100
			0.0966	0.0550	2,570
$MgA(CH_3O)(H_2O)$[a,b]	172	CH_2Cl_2	0.0887	0.0464	8,080
$MgA(CH_3O)(H_2O)$[b]		CH_3COCH_3	0.134	0.167	2,680
$MgA(CH_3O)(H_2O)$[b]		$CHCl_3$	0.0526	0.0143	1,880
$MgA(CH_3O)(H_2O)$[b]		CH_2Cl_2	0.0798	0.0376	1,490
$NiA_2 \cdot 2H_2O$	293	CH_3OH	0.182	0.587	282
$NiA_2 \cdot 2H_2O$		CCl_4	0.0815	0.0370	1,010
NiA_2	257	CCl_4	0.0708	0.0280	2,200
$CoA_2 \cdot 2H_2O$	293	CH_3OH	0.226	0.891	267

[a]Refluxed in CH_2Cl_2 prior to light scattering measurements.

[b]Since solutions prepared from this complex contain a mixture of several compounds, the $\bar{M}_w$ values only represent an indication of the extent of association.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

This has been the first work employing the Brillouin scattering technique for the determination of molecular weights of solute molecules. In addition, the portion of this research concerning the anhydrous acetylacetonate complexes in noncoordinating solvents represents the first results indicating that the solution structure of these compounds is highly polymeric. More specific conclusions follow.

1. The application of the Brillouin scattering method to the determination of the weight average molecular weight of standard Polystyrene 705 has provided additional, indirect evidence for the reliability of the "high" value of the scattering power of benzene.

2. The Brillouin method may be employed for the determination of the solution structure of small solute molecules in absorbing systems where the loss of light is as high as 60 per cent.

3. Dihydrated magnesium acetylacetonate is trans octahedral in the solid state. The corresponding anhydrous complex is monomeric in the vapor phase. In coordinating solvents, such as methanol and DMF, $MgA_2 \cdot 2H_2O$ is monomeric. In noncoordinating solvents, MgA_2 is polymeric and there is a critical dependence of the molecular weight on traces of coordinating impurities. Methylene chloride solutions of MgA_2 saturated with water are unstable with respect to the insoluble dihydrate.

4. In coordinating solvents $NiA_2 \cdot 2H_2O$ is monomeric. The anhydrous

complex, NiA_2, is polymeric in noncoordinating solvents with the molecular weight dependent upon the amount of coordinating impurities. Solutions of NiA_2 in carbon tetrachloride, when saturated with water, are unstable with respect to the insoluble dihydrate.

5. In coordinating solvents $CoA_2 \cdot 2H_2O$ is monomeric.

6. Magnesium methoxoacetylacetonate, $Mg(C_5H_7O_2)(CH_3O)(H_2O)$, is unstable in solution. The complex disproportionates to the diacetylacetonate and magnesium methoxide. On the basis of similar observations, it is believed that the cobalt and nickel analogs are also unstable in solution.

Finally, it is felt that some comments are in order with regard to the significance of the Brillouin method as applied to solution structure studies of inorganic complexes. Certainly some caution must be exercised in view of the fact that all other reported investigations indicate lower molecular weights for the compounds investigated in this work. The exceptionally high value found for MgA_2 in "dry" methylene chloride was not expected. Perhaps some colloidal $MgA_2 \cdot 2H_2O$ was partly responsible.

On the other hand, the results obtained for the nickel analog are quite reasonable from the standpoint of the method of averaging dictated by the two techniques. For a broad distribution of solute species, the number average will be considerably lower than the weight average, as is the case for NiA_2($\bar{M}n \cong 1000$, $\bar{M}w \cong 2200$).

Furthermore, the number average results obtained by other workers are typically reported in conjunction with solid state studies where the crystals investigated were obtained by sublimation and not grown from solution. It may well be that these number average molecular weight studies

were biased by the solid state results. More specifically, Cotton and Soderburg (36) reported that upon evaporation of a carbon tetrachloride solution of CoA_2 under anhydrous conditions, a glass remains as residue. This strongly suggest that the material is highly polymeric. In addition, it is known by private communication (55), that Soderberg obtained spectra for these compounds in solution that did not fit a mixture of only monomers, dimers, and trimers; however, no explanation was given.

Of the various measurements made in this work, the results obtained for polystyrene and the dihydrates were expected. It is concluded, therefore, that the interpretation of the anhydrous acetylacetonates as being highly associated is a valid one, and that the Brillouin method is quite capable of providing reasonable results for the study of such systems, especially as a complementary method to presently employed techniques that yield number averages.

Many interesting problems for research may be suggested as a result of the findings of this work. Some of those believed to be more prominant are listed.

1. It would be interesting to extend the Brillouin scattering method to higher molecular weight polymers where angular dissymmetry may be utilized for the determination of geometry and thermodynamic properties of macromolecular solutions.

2. There is a need for x-ray structure work on the MgA_2 solid. Such information could be correlated with similar work on the nickel and cobalt compounds, and could possibly shed some light on what determines the degree of association.

3. There is also a need to obtain anhydrous crystals of these compounds from solution. Presently, the only x-ray structure work performed has been on sublimed crystals.

4. The Brillouin scattering method appears to offer potential for studying the relative coordinating ability of solvents. Such a study would have to be coupled with spectral and possibly other measurements, since molecular weight determination could not distinguish between association effects and hydrogen bonding effects. Hydrogen bonding of the solvent molecules may interrupt association between solute molecules.

5. There is a need for additional number average molecular weight measurements on the anhydrous cobalt and nickel acetylacetonate, since previous measurements may have been biased.

6. Additional spectral studies are in order for the anhydrous acetylacetonates since the spectra obtained by Soderburg for these compounds were not explained.

7. It would be interesting to study more well-behaved compounds by the Brillouin method. An example would be the amine complex of cobalt acetylacetonate, CoA_2 (cyclohexylamine), which has been studied by Bertrand, et al. (86) using number average molecular weight measurements and spectroscopic techniques. They report that this compound exists solely as dimers in carbon tetrachloride and only as monomers in chloroform and methanol. In benzene a monomer-dimer equilibrium exist. In the solid state the compound is dimeric.

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*Literature references to technical journals follow the system of abbreviations as given in the Chemical Abstracts List of Periodicals, 50, 1 (1956).

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